BIOFILTRATION OF SATURATED ORGANIC COMPOUNDS: n-BUTANE AND BENZENE

By

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Butane and benzene are usually released into general working environments at low concentrations (<200 ppm). Butane is involved in tropospheric ozone development whereas benzene is a toxic compound. Biofiltration may be the best air pollution control technology for eliminating low concentrations of organic pollutants, such as butane and benzene. Thus, determinations of butane and benzene eliminations by a compost biofilter were carried out.

For butane, it was found that the acclimation period was about 40 days using an inlet concentration of 200 ppm. Butane removal efficiencies better than 90% could be maintained by a biofilter that contained a high (80%) water holding capacity (WHC) compost. However, for a low (60%) WHC biofilter compost, the butane removal efficiencies were low (< 50%). It was concluded that the butane-water absorption process may be the rate limiting factor for the removal of butane in compost biofiltration. A butane maximum elimination capacity of 18

$g.m^{-3}.h^{-1}$ and a minimum superficial residence time of 2.5 minutes were determined for compost biofilters. Butane removal rates followed first-order kinetics at low initial butane concentrations and zeroth-order kinetics at high initial butane concentrations.

For benzene elimination, it was found that the biofilter acclimation period was less than 14 days for inlet concentrations to 200 ppm. A superficial residence time of less than one minute resulted in benzene removal efficiencies greater than 90%, and maximum elimination capacity of 60 $g.m^{-3}.h^{-1}$. The rate of benzene removal followed zeroth-order kinetics which suggested that a reaction limited process was dominant for inlet benzene concentration up to 200 ppm. From batch biofilter studies, it was concluded that temperature, compost water content, pH, and their interactions had significant effects on benzene removal.

CHAPTER 1
INTRODUCTION

Objectives

The main objective of this laboratory research is to assess the operation of compost biofilters for removal of two saturated volatile organic compounds, butane and benzene. The results of these studies, based on different designs and conditions of operation, will be compared and the choice of an appropriate treatment procedure for these pollutants will be determined. Macrokinetics of pollutant elimination (purification of gas streams) for each of the two compounds will be determined in order to provide quantitative information for designing similar biofiltration systems on pilot or industrial scales. The basic operational variables of the biofilter system for these compounds may then be established.

Hypothesis

It was hypothesized that both butane and benzene eliminations by compost biofilter could be more difficult than those for higher molecular weight hydrocarbons (HCs) because butane and benzene, which are low molecular weight HCs have higher vapor pressure at ambient temperatures and are more easily evaporated than higher molecular weight HCs. The solubility of butane in water is much lower than the corresponding solubility of benzene. Biofiltration, however, consists of two consecutive processes, i.e. gas absorption into aqueous film and microbial transformation of the absorbed substances. It was also hypothesized that butane elimination by a compost biofilter could be limited by the low absorption capacity of butane rather than by microbial transformation due to the low solubility of butane in water. On the other hand, benzene elimination by compost biofilter could be limited by microbial transformation rather than by its absorption, due to its structure.

Background

The failure of many areas in the United States (U.S.) to meet the national ambient air quality standard (NAAQS) for tropospheric ozone has, over the last decade, resulted in the implementation of increasingly stringent air pollution control (APC) regulations, particularly in metropolitan areas. Since photochemically reactive volatile organic compounds (VOCs) are precursors of tropospheric ozone, VOC emissions from stationary sources, mainly industrial and commercial, have become a major target of regulations under local, state, and federal programs. In addition, even though some of the VOCs may be less or not at all photochemically reactive, they may still be toxic to humans or other living organisms, and current regulations (1990 Amendments to the Clean Air Act), therefore, may be applied to them. While these regulations typically encourage pollution prevention by the use of process changes and material substitution, such source reduction measures often will not be feasible if product quality is to be maintained. In those exceptional cases the use of APC equipment will be required to meet regulatory emission limits.

In many instances, the respective off-gas streams from stationary sources are characterized by large volumetric flow rates, particularly when the target VOCs are released into the general working environment prior to being discharged into the atmosphere. If applied to such sources, the use of established APC technologies, such as incineration, carbon adsorption and wet scrubbing, becomes technically and economically unattractive, due either to the physical and chemical limitations of the process or to the high energy cost. Moreover, health effects are of concern when employing specific APC technologies for certain compounds. For example, catalytic incineration of VOCs can only be used with well-defined waste gases due to the possibility of catalyst poisoning by certain compounds (Leson et al., 1991). Also, treatment of VOCs by chemical reaction with ozone can have secondary health effects since by-products could be harmful to the bronchial tubes.

Biofiltration is an alternative APC technology that has been introduced for diluted waste gas purification. The principle of this technique, which is used to clean volatile pollutants from the gas stream, is the utilization of microorganisms inside thin water films attached to the filter media. Even though biofilters were originally applied only to control odorous off-gases from sewage treatment and rendering plants (Bohn, 1975; Ottengraf, 1977; Prokop and Bohn, 1985; Terasawa et al., 1986; Bohn and Bohn, 1987; Eitner and Gethke, 1987; Frechen and Kettern, 1987), they are now being used successfully for the control of volatile organic compounds (VOCs) and air toxics from a variety of sources (Don, 1985; Ottengraf et al., 1986; Kampbell et al., 1987; Ebinger et al., 1987; Kosky and Neff, 1988; Janssen et al., 1989; Ergas et al., 1991; Leson and Winer, 1991). Because of the inherent advantages associated with biofilters, detailed investigations of their operation in the control of odorous off-gases, VOCs or air toxics have increased considerably in recent years.

In the U.S., a number of investigations of the operation of biofilters has been carried out (Bohn and Bohn, 1987; Ebinger et al., 1987; Ergas et al., 1991; Leson et al., 1991; Yang and Allen, 1991; Yang, 1992; Allen and Yang, 1991). However, these biologically based systems have not received as much attention in the U.S. as in European countries, particularly in applications for purifying organic toxic compounds.

From an environmental viewpoint, as well as for economic reasons, the low specific energy consumption of biofilters is one of their most attractive features. Unlike most other air pollution control technologies, biofiltration does not generate undesirable gaseous by-products (such as NO_x from incineration) or hazardous waste. As long as the original filter material is not initially contaminated (e.g., with heavy metals) the spent material can be disposed of as a nonhazardous waste or mixed with compost for other applications.

Research activities related to laboratory-scale systems and practical full-scale applications of the technology are currently under way in the U.S. These studies are directed towards developing a better understanding of the parameters that affect the biodegradation of air pollutants and to demonstrate the applicability of biofiltration to a broad range of industrial emission sources. Similarly, it is now being recognized in the U.S. that biofiltration is a potentially important and innovative approach to control large volumes of low concentration off-gases, especially for volatile organic compounds and carcinogenic air pollutants (Kosky and Neff, 1988; Leson and Winer, 1991; Leson et al., 1991). Because volatile organic compounds, such as butane and benzene, which are produced industrially and used commercially, have the ability to be toxic to humans (carcinogenic) as well as being precursors for tropospheric ozone development, studies directed at the use of biofiltration for VOCs control are very important.

Gordon et al. (1968) determined the average concentration of butane in the Los Angeles atmosphere in the fall of 1967 and found values in the range of 132 to 304 ppb. Altshuller et al. (1971) conducted a similar study and concluded that butane appears to arise from sources other than those responsible for pentanes or fuel hydrocarbons. Recently, butane concentrations in the troposphere have been measured in several cities in the U.S., and the effect on tropospheric ozone as a precursor was estimated (Chameides, et al., 1992). Chameides et al. reported that of the top 35 species of all hydrocarbons measured at the Georgia Institute of Technology campus, Atlanta, (1100-1400 LT) from July 13 till August 3, 1991, the average n-butane concentration was the second highest (16.9 ppbC) and benzene was sixth in concentration (8.8 ppbC). For species sorted by OH reactivity, butane was eighteenth (1.7 Propylene Equivalent ppbC) in the list of 35 species. Also, these researchers reported reactivity in terms of the number of molecules of ozone produced per C atom of species oxidized. Based on this categorization, butane can produce 0.34 molecules of ozone for every single carbon atom in butane. Benzene, on the other hand, can produce only 0.11 molecules of ozone per carbon of benzene. This assessment indicates the importance of butane as a precursor of tropospheric ozone.

For benzene, the reason for studying this component is clearly not its reactivity as a precursor for tropospheric ozone development but rather its health effects. For example, benzene is suspected to be carcinogenic, and therefore it should be strictly regulated. Emission of benzene into the atmosphere at any level should be avoided, and therefore it is included in the list of air toxics to be regulated under Title III of the 1990 Amendments to the Clean Air Act. Butane, on the other hand, is not included in the air toxics list (Title III 1990

Clean Air Act Amendments); however, in several states, it is included in the substances list of health risk documents. For example, the office of environmental health hazard assessment (OEHHA) of the State of California includes both benzene (emittent ID: 71432) and butane (emittent ID: 106978) in its substances list of the OEHHA Health Risk Assessment Summary Documents (State of California-EPA, 1993). The health effects observed on exposure to butane are known to be not as serious as those for benzene even though some experiments carried out on animals have indicated possible health effects. The importance of butane in this study, however, is mainly a consequence of its effect and contribution to the development of tropospheric ozone.

From the point of view of biofiltration, elimination of both butane and benzene using a compost biofilter has not been demonstrated. One study has been conducted on a mixture of butane, propane and isobutane (Johnson and Johnson aerosol propellant) by Kampbell et al. (1987). However, the filter media used in the published study was soil (soil bed biofilter). Ottengraf et al. (1986) conducted an experiment on the elimination of benzene through suspended growth experiment but benzene elimination using biofiltration has not yet been reported. More quantitative information is needed in order to compare elimination of benzene with the elimination of butane, which is a saturated aliphatic hydrocarbon.

Thus, the choice of butane and benzene for this study was a result of their health effects, their propensity as precursors for tropospheric ozone formation and the lack of quantitative information regarding their elimination using compost biofilters. The results obtained in this work will provide an understanding of the elimination of a light aliphatic straight chain hydrocarbon (butane) and the fundamental aromatic hydrocarbon (benzene).

Hutzinger and Veerkamp (1981) classified degradability of organic compounds based on their structures, as presented in Table 1-1. Saturated hydrocarbons with low molecular weight are less degradable than those with higher molecular weights. However, the lower alkanes are more degradable than aromatic hydrocarbons. From the categorization described in Table 1-1, butane, which is a low molecular weight alkane hydrocarbon, will be more degradable than benzene, an aromatic hydrocarbon. However, butane is less soluble in water than benzene. Therefore, it is hypothesized that a difficulty in elimination of butane by biofiltration could be due to a low absorption coefficient in water, whereas that for benzene could be due to its structure, which is related to its reactivity or capacity for transformation. From the experimental results of this work, it should be possible to determine whether absorption or biological transformation will be the primary rate-determining step in the elimination of each of these hydrocarbons.

Review of Literature

General

Biological waste gas purification can be divided into 2 (two) consecutive processes. The first step is the absorption of the waste gas components in water (water film), and the second step is microbial transformation of the absorbed substances with the consumption of oxygen. These two processes can be carried out at the same location or at different locations in the liquid film. The reactors in which these two processes can occur at different locations are called bioscrubbers, whereas the reactors in which the processes occur at the same

Table 1-1. Influence of chemical structure on degradability.

Types of compounds	More degradable	Less degradable
Hydrocarbons	Higher alkanes (≥12)	Lower alkanes
	Alkanes	Higher molecular weight alkanes
	Straight-chain paraffins	Branched-chain paraffins
	Paraffins	Aromatic
	Mono- and bicyclic aromatic	Polycyclic aromatic
Aromatic substituents	-OH	-F
	-COOH	-Cl
	-NH_2	-NO_2
	-OCH_3	-CF_3
		-SO_3H
Aliphatic chlorine	-Cl more than 6 C atoms from terminal C	-Cl 6 or less C atoms from terminal C

Source : Hutzinger and Veerkamp in Microbial degradation of xenobiotics and recalcitrant compounds (Leisinger et al., 1981).

location are called biofilters and drip units or trickling filters.

There are differences and similarities between a drip unit and a biofilter. The differences are in the amount of water added and in the microbial support provided. In a biofilter, just enough water is fed to the biofilter to insure a sufficient moistening of the microbial support, whereas in a drip unit, water flows through the bed continuously and is recycled. A biofilter requires a very large support on which microorganisms are finely distributed around the filter media (support materials). On the other hand, the surface of the support for a drip unit is relatively small, and the layer of microorganisms is very thick (biological lawn). The small number of microorganisms in a biofilter will limit the gas velocity to be used (to provide an adequate residence time), whereas the supply of oxygen to the "biological lawn" in a drip unit is rate determining. In addition, plastic packing materials are commonly used in drip units as supports, and special nutrients for the microorganisms must be added to the water. For a biofilter, the nutrients are added only if necessary, since the filter support media, such as compost or some other organic material, are usually rich in necessary nutrients. The addition of nutrients to a biofilter if necessary may be accomplished by treating the water moistening system. The similarities between biofilters and drip units are that both units employ a single reactor for absorption and transformation of waste gas components and that the average rate of flow of pollutant gas into these two reactors is very low.

Thus, biofiltration is a technique based on the ability of microorganisms to simultaneously degrade several waste gases, organic as well as inorganic compounds, to mineral end-products, such as water, carbon dioxide, salts, and microbial biomass (Ottengraf, 1987; Dharmavaram, 1991). A biofilter consists of one or more beds of biologically active material, primarily mixtures based on compost produced from a variety of raw materials, including municipal solid waste, wood chips, and bark. Inert materials, such as polystyrene particles, perlite and clay, are frequently added (Ottengraf et al., 1984; Dragt et al., 1987; Paul and Castelijn, 1987). Filter beds ranging from 3 to 4 feet in height are very commonly used (Ottengraf et al., 1984; Dharmavaram, 1991).

Waste gas treatment involves procedures where the contaminated off-gas is collected and vented from the emitting source, usually into an air distribution system at the bottom of the filter bed. The target pollutants are removed from the off-gas stream on its way through the filter bed by diffusion into a wet film covering the filter particles (Ottengraf and van den Oever, 1983; Ottengraf et al., 1984; Ottengraf et al., 1986; Ottengraf, 1987). Microorganisms, which are present in the filter material (Leson et al., 1991; Yang, 1992) or have been added using appropriately cultured/inoculated microbial consortia into the filter material (Don, 1985; Ottengraf et al., 1986; Bijl et al., 1987), are immobilized in a liquid phase film attached to the filter material. The liquid phase is formed by water, which is adsorbed and attached to the filter material. The pollutants, which pass from the gas into the aqueous phase, will be degraded aerobically by the microorganisms to form carbon dioxide, water and salts.

A filter bed using appropriate natural filling material, such as compost, can be a good medium for microorganisms to grow on its solid surfaces. The compost not only acts as an environmentally compatible support but can supply microorganisms with inorganic nutrients for food. Many organic compounds present in the waste gas are absorbed in the liquid phase of the bed and eliminated biologically because they can serve as a readily available carbon source for the microorganisms (Bohn and Bohn, 1987; Ottengraf, 1987; Dharmavaram, 1991). The composition of the solid phase support and the population of viable organisms present can be optimized such that aging can be prevented, and a relatively high activity can be maintained for a long period of time (years).

Biofiltration of Organic Compounds

Considerable progress has been made in the biological purification of waste gases. The use of biofiltration for purifying organic pollutants has mainly been applied in Europe, particularly in Germany (Bohn, 1975; Brauer, 1986; Frechen and Kettren, 1987; Leson and Winer, 1991) and the Netherlands (Ottengraf et al., 1986; Bijl et al., 1987; Dragt et al., 1987; Paul and Castelijn, 1987; Janssen et al., 1989). Also, in the U.S., studies of biofiltration for purification of odorous waste gases and organic compounds have received some attention (Prokop and Bohn, 1985; Bohn and Bohn, 1987; Kampbell et al., 1987; Leson et al., 1991; Yang, 1992; Allen and Phatak, 1993).

Unlike odorous gases, such as H_2S, organic compounds are basically difficult to degrade using a biofilter. The ability of microorganisms to degrade organic compounds in a biofilter is strongly dependent upon the types and concentrations of the compounds. Ottengraf (1987) classified organic compounds into two main classes: biogenic (natural origin) and anthropogenic (man-made origin). These two classes of organic compounds were based on their specific sources because it was believed that the biodegradability of organic compounds generally reflected their sources. Biogenic organic compounds can generally be degraded easily because of the existence of naturally occurring enzymatic systems that have been developed by microorganisms. Conversely, anthropogenic organic compounds are basically difficult to degrade microbiologically unless an enzymatic system containing appropriate microorganisms can be created.

Anthropogenic organic compounds are classified into two groups: synthetic natural products and xenobiotics. Xenobiotic organic compounds are compounds that are unrelated to life. Xenobiotic organic compounds are categorized into three classes based on the levels of their biodegradability, i.e., weakly xenobiotic (easily degraded compounds), recalcitrant compounds (not easily degraded compounds), and persistent compounds (nondegraded compounds).

Ottengraf et al. (1986) in the Netherlands conducted experiments on biological elimination of volatile xenobiotic compounds using biofilters. Several xenobiotic compounds were tested for their potential biodegradability. These tests were done in aqueous batch systems under aerobic condition (in shaking flasks). Inoculum was made using activated sludge, contaminated soil or monocultures of bacterial strains from previous investigations. Microbial degradation of the compounds was checked by measuring the concentration of the compounds as a function of time. Selection and isolation of the appropriate microorganisms were carried out using an enrichment culture technique.

Using this method, biodegradability was tested for a number of volatile organic compounds, such as dichloromethane, 1,2-dichloroethane, xylene, styrene, methyl acrylate, dimethyl formamide, acrolein, thioacetic acid, acrylonitrile, etc. The enriched cultures obtained served as inoculum for the packing material when applying biofiltration to purify waste gases contaminated with these compounds.

The results of Ottengraf and coworkers' experiments showed that dichloromethane (CH_2Cl_2) could easily be eliminated by microorganisms isolated from activated sludge. This compound was also eliminated by the bacterial strain Hyphomicrobium, GJ21, which was isolated at the Groningen Biotechnology Center, The Netherlands. Essentially, it was found that organic chlorine could be microbiologically converted to inorganic chlorine. The bacterial strain Xanthobacter autotrophicus, GJ10, which also was isolated at the Groningen Biotechnology Center, could eliminate 1,2-dichloro ethane (CH_2ClCH_2Cl). 2-Chloro ethanol was formed as an intermediate, the methylene chloride was degraded via chloro acetaldehyde and chloroacetate to glycolate. Organic chlorine was converted to hydrogen chloride as indicated by decreasing pH. It was suggested that this strain might be able to eliminate all terminally monohalogenated C1-C4-alkanes by conversion to the corresponding alcohols.

Xylene ($C_6H_4(CH_3)_2$) and styrene ($C_6H_5CH{:}CH_2$) could be eliminated by bacterial strains isolated from activated sludge. The isolated strains all belong to the genus Nocardia, and each strain was found to be able to use the other three compounds as substrates. Dimethyl formamide ($(CH_3)_2NCHO$) could be eliminated by microorganisms isolated from activated sludge. A two-step elimination occurred: First, dimethyl formamide was hydrolyzed to dimethylamine and formic acid, and second, formic acid was oxidized to CO_2 and H_2O. Also, dimethylamine was oxidized to CO_2, H_2O and ammonia. Dimethylformamide was used as a carbon and energy source as well as a nitrogen source.

Ammonia could be oxidized via nitrite to nitrate by microorganisms from the genera Nitrosomonas and Nitrobacter. Thioacetic acid (CH_3COSH) could easily be eliminated by microorganisms isolated from activated sludge. It was hydrolyzed to acetic acid, and H_2S was oxidized to CO_2, H_2O and sulfuric acid. Carbon disulfide (CS_2) was not eliminated by microorganisms from activated sludge without the addition of another carbon source. When another carbon source, such as alpha-D-glucose, methanol or formic acid was added, CS_2 was eliminated but very slowly. Since no sulfite or sulfate could be detected, CS_2 was used only as a sulfur source.

Propenal (acrolein, CH_2:CHCHO) could not initially be eliminated by microorganisms present in activated sludge. However, it was possible to grow microorganisms isolated from activated sludge on propanal as a sole carbon source. Therefore, culture solution containing propanal as a carbon source was increasingly added with a very small amount of propenal until the ratio of propenal to propanal in the solution had increased considerably, and finally, propenal replaced all propanal and remained in the solution as a sole carbon source. Microorganism strains were also isolated for the elimination of acrylonitrile (CH_2:CHCN), benzene (C_6H_6), methyl acrylate (CH_2:$CHCOOCH_3$), and formaldehyde (H_2CO).

In order to make biofiltration applicable on a larger scale to process industry, it is necessary to find microorganisms that are able to eliminate compounds that are unrelated to life (xenobiotics). Easily degradable compounds need only natural filter materials, but xenobiotic compounds require inoculation with specially cultivated organisms. In general, the biodegradation of xenobiotics will be enhanced if the waste gas stream has simple composition. Gases containing several different biodegradable and xenobiotic compounds need multistage filter beds, where a certain stage of the filter bed will provide optimal growth conditions for specific microbial populations.

Ottengraf et al. (1984) have used a peat-compost biofilter to remove synthetic wastes of organic compounds consisting of toluene (460 $g.L^{-1}$), ethylacetate (157 $g.L^{-1}$), butylacetate (121 $g.L^{-1}$), and butanol (56 $g.L^{-1}$) in a two year investigation. The peat-compost biofilter medium was found to have a high VOC removal rate and provided a low pressure drop. After a ten day acclimation period, zero order kinetics were observed for the substrate concentrations used. The maximum elimination capacity for the bed was about 20-40 $g.m^{-3}.h^{-1}$ for the compounds present. After a two week period of inactivity, loss of microbial activity in the filter bed was negligible.

Bijl (1987) conducted experiments on biofiltration of pollutants emitted from a pharmaceutical industry. Three sections of a biofilter containing 60 m^3 of specially prepared filter material were installed, for pollutant purification from a pharmaceutical factory, having 20 m^2 surface area and 7 m total height. Two sections were inoculated with microorganisms to eliminate ethyl alcohol and isopropanol. The top section was inoculated with special microorganisms to eliminate dichloroethane. The load of the system was 5000 m^3 of process air per hour. The concentrations of ethyl alcohol, iso-propanol and dichloroethane entering the system were 5300, 4915 and 5210 $mg.m^{-3}$, whereas the corresponding concentrations in air leaving the system were 33, 10 and 890 $mg.m^{-3}$, respectively.

Dragt et al. (1987) conducted experiments on the biological treatment of waste gases from small urban sources that emitted volatile organic compounds. A pilot plant scale system with the patented name Bioton^R was installed at a lacquer plant to control emissions resulting from printing and lacquering of wood, which included plastic solvent vapors. The organic compounds released were mainly toluene, ethylacetate, butylacetate, ethanol, isopropanol, and butanol. The gas stream load of 1000 $m^3.h^{-1}$ with a relative humidity of 100% was treated using this system. About 650 $m^3.h^{-1}$ of the solvent vapor loaded gas stream was fed to a carbon adsorber to prevent extreme concentrations of the volatile organic components in the waste gas from reaching the inlet to the biofilter. The water content was adjusted to about 40 - 60% on a weight basis in the packing material. Packing material used consisted of a mixture of compost and inorganic additives. Using this packing material the load could be increased up to 10 times more than that using compost alone at the same pressure drop.

The results of these experiments were as follows. In the first two weeks a low load of 100 $m^3.m^{-2}.h^{-1}$ was used. This load was increased to 200 $m^3.m^{-2}.h^{-1}$ for the rest of the investigation, when the system was found to be running well. A pressure drop of 60 Pa at 200 $m^3.m^{-2}.h^{-1}$ was measured. The elimination capacity was found to be a function of the gas concentration at low organic loadings of the biofilter. For a gas concentration more than 750 mg $C.m^{-3}$, the elimination capacity was maximal at 35 g $C.m^{-3}$-h^{-1}. As a general conclusion they stated that biofiltration was applicable for the control of off-gases containing volatile organic compounds (VOCs) as well as odorous gases. Combinations of biofilters with other accumulation techniques, such as carbon adsorption, is very useful if the emission pattern is intermittent. The cost of the biofilter is low compared with other traditional techniques. Biofiltration is a clean technology because the pollutants removed are not drained into other streams.

Paul and Castelijn (1987) tested a patented filter material and a patented biofiltration reactor. The filter material, called Vamfil, was a mixture of organic materials (tree bark and compost and added nutrient). After inoculation, the Vamfil material could degrade toluene with a maximum break-down capacity of 200 g toluene.m^{-3} Vamfil.h^{-1} at 40°C. The biofilter reactor, designed by Comprimo Engineers & Contractors and called BIOBOX, guaranteed optimum process conditions to ensure the effectiveness of the microorganisms in order to reduce a high degree of odor and to remove effectively hydrocarbons contained in the off-gas streams. A breakdown capacity of 200 g C.m^{-3} Vamfil.h^{-1} was reported. This reactor provided high reliability, low operating and investment costs and easy maintenance.

Eitner and Gethke (1987) found that organic compounds that were well sorbed and easily biodegraded were eliminated through biofilters. Compounds that were not well sorbed, but well degraded were also eliminated. However, compounds that were not well degraded (dioxin, dichloromethane, trichloroethane) had low removal efficiencies. It was mentioned that the addition of 5% activated carbon to the biomass significantly increased the removal efficiency for well-degraded substances.

Don (1985) carried out an investigation of the optimization of a compost bed for reducing resistance to flow. By modifying the particle size distribution, a material was developed with about 10 times lower resistance to flow than the original material. Essentially the particle size distribution was modified by mixing the fairly fine active fraction of the compost with the coarse inactive particles either from the compost or from other materials. When used in a 5 m^3 pilot plant installation the filter material proved to have a good stability, i.e., the pressure drop after one year of operation at 300 $m^3.m^{-2}.h^{-1}$ for a bed height of 1 m was not greater than 450 Pa (45 mm water). As a result, the treatment cost was reduced to about 50% of normal, and the installation size was reduced to one third of its original dimensions because of a higher surface loading rate. Four industrial installations have been placed in operation with good results. The results for the degradation of a number of organic components, such as toluene, in pilot plant scale biofilters having the dimensions, 1.0 m height and 0.5 m diameter, were also reported. Degradation efficiencies of up to 90% for toluene were achieved by adjusting the surface load so as not to exceed 25 $m^3.m^{-2}.h^{-1}$. However, by addition of inorganic nutrients the degradation could be enhanced dramatically, i.e., at about 300 $m^3m^{-2}.h^{-1}$ surface load, the efficiency could be maintained at greater than 90%.

Coordinated research activities on biofiltration have been made in the California South Coast Air Basin (SoCAB) (Leson et al., 1991). Activities included bench-scale testing of ethanol emissions, pilot testing of ethanol emissions from large bakery ovens with a mobile biofilter unit, and construction and performance evaluation of a full-scale biofilter demonstration unit for ethanol emission from a local investment casting operation. The bench-scale experiments were conducted at the University of Southern California.

Off-gas with known concentrations of ethanol was vented through PVC columns 7.6 cm in diameter and 100 cm in height. The filter material was composted park waste. Ethanol concentrations were measured in the raw gas at six equidistant locations in the filter with a gas chromatograph/flame ionization detector (GC/FID) system. Inlet concentrations of ethanol in the raw gas were 1000 - 4000 $mg.m^{-3}$ (500 - 2000 ppm). The maximum elimination capacity was found to be 100 $g.m^{-3}.h^{-1}$ and followed zero order elimination kinetics. Pilot testing of biofilters for ethanol emissions from bakeries was conducted with a 3.6 m x 2.4 m x 2.55 m fully enclosed and insulated metal container. The filter bed was 2 m^3 volume and 1 m in height. An off-gas flow rate of 1250 $m^3.h^{-1}$ was treated. Moisture control was provided by load cells that determined the weight of the filter material and indicated when a lack of moisture occurred. The full-scale unit was planned for ethanol control from an investment casting facility with a filter area of 210 m^2 and filter volume of 273 m^3. Maximum off-gas flow was 17,000 $m^3.h^{-1}$.

Ebinger et al. (1987) conducted laboratory experiments and investigated the industrial applications of soil bed biofilters. The filter material, consisting of about 100 grams of soil with particle diameters less than 2 millimeters, was placed inside 0.95 L canning jars in the laboratory experiments. Moisture contents and temperatures of the filters were adjusted to 1-2%, 10%, 20% and 2°, 15°, 20°, 25°C, respectively. At a pH in the range 6-8, these investigators found that 1 - 3% propane concentrations in the air stream could be reduced to one half by passage through the soil bed biofilter for residence times from 5 to 20 hours. Propane removal was found to be slower when the temperature and pH of the filter were 2°C and 5.3, respectively. Removal efficiencies in the range of 92 to 98% were found for propane concentrations in the range of 0.6 to 1.0 %. The soil bed experiments used fine sandy loam containing 15% clay and 0.8 % organic matter. The reactor was made from PVC pipe, 10 cm in diameter and 1 m in length, which was buried horizontally about 50 cm below the soil surface. The air flow containing propane was passed through the soil bed at 800 $m^3.h^{-1}$ or 500 cfm. It was found that generally the propane removal rate increased when the temperature increased, but in the range from 20° to 30°C the propane removal rate was the same. When the soil water content was low the propane removal rate was low. However, for a moisture content of 10% the propane removal rate was faster than at 20%. They concluded that faster gas exchange occurred in the soil at 10% moisture content than at the

20%. The soil bed's removal efficiency for propane in summer and winter was observed to be in the range of 92 to 98%.

Kampbell et al. (1987) investigated removal of propane, isobutane, and n-butane from a waste air stream in laboratory studies and in a prototype soil bioreactor. The prototype system was used to purify aerosol propellant, which was released during the filling process. Native soil was used as the filter medium and a geotextile liner was installed below the bed for the protection of groundwater. Laboratory investigations indicated first-order kinetics and the potential to degrade light aliphatic hydrocarbons and trichloroethylene, a compound ordinarily resistant to aerobic biological treatment. Predicted behavior of the bioreactor, based on laboratory studies, agreed closely with the actual behavior of the field system. The prototype bioreactor reduced the hydrocarbon concentrations in the waste air by at least 90 % with a residence time of 15 minutes and a pressure drop of 8500 Pa (85 cm of water). Use of the geotextile liner caused high moisture conditions in the lower part of the bed and corresponding loss in VOC removal capacity. The biofilter functioned well in the temperature range of 12° to 24°C. However, during the extreme winter temperatures experienced at Racine, Wisconsin, the removal efficiency of VOCs diminished significantly.

Properties of Butane and Benzene

Butane or n-butane, C_4H_{10}, is a flammable gas that boils at -0.5°C. It is slightly soluble in water (61 $mg.L^{-1}$ at 20 °C and standard pressure). The molecular weight is 58.12.

Benzene with a molecular formula of C_6H_6, is a clear, colorless, highly flammable liquid. It has a low boiling point and high vapor pressure at ambient temperatures. Benzene is soluble in acetone, carbon tetrachloride, ether, chloroform, alcohol, carbon disulfide, glacial acetic acid and numerous other organic substances. It is a cyclic aromatic hydrocarbon that is highly refractive, nonpolar and nonreactive with low viscosity and low surface tension.

As a result of its structure, benzene is a stable compound. Some typical benzene reactions require high temperature and pressure in the presence of catalysts. Common reactions are sulfonation, hydrogenation, nitration, chlorination and bromination.

At standard temperature and pressure benzene is in liquid form. Molecular weight is 78.11. It can melt at 5.53°C (42°F) and boil at 80.1°C and 760 mm Hg. Vapor density (air=1) is 4.0 at 90°C, and vapor pressure is 75 mm Hg at 20°C. Solubility in water is 0.178% by weight at 20 °C and standard pressure (1780 $mg.L^{-1}$). Air saturated percent benzene at 760 mm Hg and 26°C is 13.15. Density of a saturated air/benzene mixture is 1.22 at 760 mm Hg; 26°C relative to air (1.0).

Sources and Production of Butane and Benzene

Butane is a saturated aliphatic hydrocarbon occurring in natural gas. The presence of butane in the atmosphere is attributed to natural gas leakage, petroleum gas leakage, or diffusion through the soil from petroleum deposits (Aviado, et al., 1977). Liquefied petroleum gas, otherwise known as LP gas or simply LPG, is produced by the oil industry from a mixture of petroleum hydrocarbons consisting mainly of propane and butane. The mixture is occasionally defined more definitively as LPG-butane, LPG-propane, mixed LPG, unsaturated LPG, etc., indicating a predominance of one or more of the chemical species. The growth of LPG consumption over the last twenty years has been remarkable. Statistics indicate that the global use of LPG has risen from 31.8 million tons in 1960 to 65.3 million tons in 1970; this implies an annual percentage growth of 6% in the U.S.A. and near 28% for other countries (Williams and Lom, 1974).

Until recently, fluorocarbons were the major propellants used in the aerosol industry. However, the potential environmental hazards associated with the use of fluorocarbons and other considerations have made it necessary to develop aerosols using hydrocarbons as propellants. Propellant mixtures consisting of propane, butane and isobutane are becoming important because they represent a means of continuing to use aerosol spray devices without fluorocarbons.

The production of benzene in the U.S. is principally affected by the petroleum and petrochemical industries (≈ 95%) and from coal-derived benzene (≈5%). For example, catalytic reformation produces 67% of the total benzene produced in the U.S. Pyrolysis of gasoline contributes about 10% and hydrodealkylation of toluene produces another 10%. Toluene disproportionation gives 8 % and coal-derived benzene, which is benzene from coal via carbonation to crude light oil, contributes 5% of the total benzene produced in the U.S.

Benzene is used as an additive to increase the octane rating of unleaded gasoline. It is also utilized as a solvent and reactant in laboratories, in the manufacture of pesticides, paint removers, rubber cements and detergents. In fact, the usage of benzene and its derivatives has become so widespread that there really is no facet of our lives today that is not touched by used of these compounds.

Health Effects of Butane and Benzene

Shugaev (1969) determined the concentration of butane that kills 50% (LC_{50}) of mice and rats. The LC_{50} is 680 $mg.L^{-1}$ for mice (exposed for 2 hours) and 658 $mg.L^{-1}$ for rats (exposed for 4 hours). The effective concentration of butane, at the LC_{50} level, in the mouse brain is 77.9 $mg.100^{-1}.g^{-1}$. The following concentrations of butane were also found in various tissues of rats: 75.1, 49.2, 44.1, 52.2 and 208.6 $mg.100^{-1}.g^{-1}$ in brain, liver, kidneys, spleen, and perinephric fat, respectively.

The effect of butanes and pentanes on the central nervous system (CNS) was studied by Stoughton and Lamson (1936). They found that butane in a concentration of 13% v/v produced light anesthesia within 25 minutes in mice, and only one minute was required to induce the same effect with 22% concentration. Also, this concentration produced loss of posture within 15 minutes. Isobutane, on the other hand, in concentrations of 15%, 20%, and 23% produced light anesthesia in mice within 6, 17, and 26 minutes, respectively. For a concentration of 35%, however, isobutane induced loss of posture in mice in 25 minutes. These researchers concluded that branched isomers of the alkane series are less active and less toxic than straight chain compounds.

Irradiated butane has been reported to cause eye irritation. The average threshold time for eye irritation of individuals exposed to 2 ppm of irradiated butane was 240 seconds (Heus and Glasson, 1968). The concentration of butane that would have a noticeable odor is 5.24×10^{-5} $mole.L^{-1}$ or 3.05 $mg.L^{-1}$. Butane, among other n-alkanes, has a pronounced inhibitory effect on the growth of bacteria, actinomycetes, fungi, algae and plant seeds, chick embryos and the various states of metamorphosis of the fruit fly (Rode and Forster, 1966).

Benzene is one of the compounds that is regulated as an air toxic in Title III 1990 Amendments to the Clean Air Act. Benzene is not as reactive as butane in terms of reactivity as a photochemical ozone precursor. However, the health effects of benzene are sufficient cause for concern, justifying regulation. When benzene enters the body, it can act as a bone marrow poison, and it is suspected to be a cause of leukemia. Acute exposure to benzene can affect the control of the nervous system (CNS), and chronic exposure can result in damage to the blood-forming system. Benzene can enter the body through ingestion, inhalation and skin absorption. Direct contact with the skin can cause congestion in the capillaries and then produce a reddish color, known as erythema. More progressive conditions of benzene exposure can produce blisters, and continuous contact with benzene can result in skin drying that becomes a scale. Mucous membranes of the eyes, nose and lungs are irritated by high ambient air concentrations of benzene.

Kinetics

Kinetic relationships specific to biofiltration have been developed by several researchers. For example, Ottengraf and van den Oever (1983) and Ottengraf (1986) have developed kinetic equations for biofiltration and assumed that both diffusion and reaction affect the removal of the pollutants. In developing the differential expressions, they considered either zeroth- or first-order reactions. However, based on the experimental investigations, the zeroth-order microkinetics are often encountered in the degradation of many common volatile pollutants. Then, they classified the zeroth-order reaction into two categories: (1) reaction limitation and (2) reaction and diffusion limitations.

Figure 1-1 shows the progressive elimination of pollutants through biofiltration. At steady state, the differential equation describing the mass balance for a compound, C_l, in the liquid layer of the biofilm is given as the following expression.

$$D' \frac{d^2C_l}{dx^2} - R = 0 \tag{1-1}$$

where D' is effective diffusion coefficient and R is the reaction rate due to biodegradation. The reaction rate commonly described by the Monod substrate utilization expression is

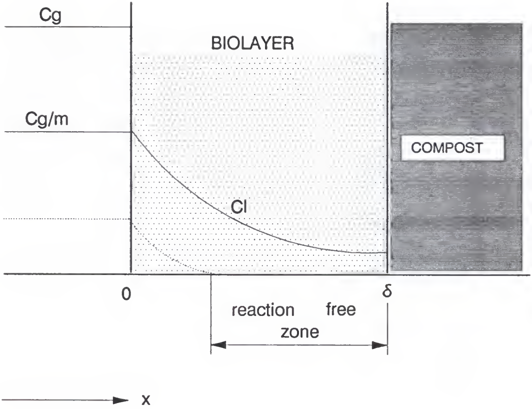
$$R = (\mu_{max} \rho_b) \frac{C_l}{K_s + C_l} \tag{1-2}$$

where μ_{max} is the maximum specific growth rate of the biomass, K_s is the substrate saturation constant and ρ_b is the biomass density. Two conditions are commonly applied in equation (1-2). First, at $K_s \lll C_l$, the rate expression approaches zero-order kinetics in the substrate concentration, and equation (1-2) becomes

$$R = k_0 \tag{1-3}$$

where $k_0 = \mu_{max}\, \rho_b$. Second, at $C_l \lll K_s$, the Monod expression reduces to a first-order rate expression, and it can be written as the following equation.

$$R = k_1 C_l \tag{1-4}$$



Cg : gas phase concentration
Cl : liquid phase concentration
m : distribution coefficient
δ : total biolayer thickness
x : length coordinate

Figure 1-1. Graphical representation of biophysical model for the biofilter.

where $k_1 = (\mu_{max}\ \rho_b)/K_s$.

Zeroth-order Reaction Rate

When a zeroth-order reaction rate from equation (1-3) is substituted into the differential equation (1-1), the following expression is found.

$$D' \frac{d^2 C_l}{dx^2} - k_0 = 0 \tag{1-5}$$

Ottengraf and van den Oever (1983) and Ottengraf (1986) distinguished two situations for this zeroth-order rate condition. First, there is no diffusion limitation in the wet biolayer, and therefore the conversion rate is only controlled by the reaction rate, which they refer to as "reaction limitation". Second, if diffusion limitation occurs in the wet biolayer, this means that the depth of penetration, λ, in the biolayer is smaller than the thickness, δ, of biofilm. Therefore, the conversion rate is controlled by the rate of diffusion which is referred to as "diffusion limitation."

Reaction limitation

For the situation when reaction limitation occurs, equation (1-5) can be solved with the following boundary conditions (BCs).

$$x = 0, \qquad C_l = \frac{C_g}{m} \qquad 1\text{-}6)$$

$$x = \delta, \qquad \frac{dC_l}{dx} = 0 \tag{1-7}$$

By integrating equation (1-5) and applying the BC of equation (1-7), the following differential equation is found:

$$\frac{dC_l}{dx} = \frac{k_0}{D'}x - \frac{k_0}{D'}\delta \tag{1-8}$$

Similarly, by integrating equation (1-8) and applying the BC of equation (1-6), the following expression can be found:

$$\frac{C_l}{C_g/m} = \frac{k_0\, m}{2D'C_g}x^2 - \frac{k_0\, m\, \delta}{D'C_g}x + 1 \tag{1-9}$$

Since $\sigma = x/\delta$ (the dimensionless length coordinate in the biolayer) and $m = C_g/C_l$ (distribution coefficient), equation (1-9) can be written in the following form:

$$\frac{C_l}{C_g/m} = 1 + \frac{1}{2}\,\frac{k\, m\, \delta^2}{D'C_g}\,(\sigma^2 - 2\sigma) \tag{1-10}$$

By definition,

$$\phi^2 = \delta\sqrt{\frac{k\, m}{D'C_{go}}} \tag{1-11}$$

which is the Thiele Number. Substituting equation (1-11) into equation (1-10), the following expression is found:

$$\frac{C_l}{C_g/m} = 1 + \frac{1}{2}\,\frac{\phi^2}{C_g/C_{go}}\,(\sigma^2 - 2\sigma) \tag{1-12}$$

Gas phase mass balance is given in equation (1-13) as follows:

$$-U_g \frac{dC_g}{dz} = N\,A_s \tag{1-13}$$

where U_g is gas velocity, C_g is gas concentration, z is column height, N is substrate flux into the biolayer and A_s is biolayer surface per volume. The value of N is

$$N = \frac{-D'}{\delta}\left(\frac{dC_l}{d\sigma}\right)_{\sigma=0}$$

and since $\sigma = x/\delta$, this equation can be written in the following form:

$$N = \frac{-D'}{\delta}\left(\frac{dC_l}{dx}\right)_{x=0} .\,\delta \tag{1-14}$$

Substituting equation (1-8) into equation (1-14), the value of N can be simplified as given in equation (1-15):

$$N = k\,\delta \tag{1-15}$$

Combining equation (1-13) and equation (1-15), the following differential equation is produced:

$$\frac{dC_g}{dz} = -\frac{k_0\,\delta\,A_s}{U_g} \tag{1-16}$$

With the BCs,

$$z = 0, \qquad C_g = C_{go} \tag{1-17}$$

$$z = Z, \qquad C_g = C_{g-e} \tag{1-18}$$

By integrating equation (1-16) and applying the BCs in equation (1-17) and equation (1-18), the ratio of exit and inlet gas concentrations through the biofilter are found to have the following relationship:

$$\frac{C_{g-e}}{C_{go}} = 1 - \frac{A_s\ k_0\ \delta\ Z}{C_{go}\ U_g} \tag{1-19}$$

where, C_{g-e} is concentration of the gas at the exit, C_{go} is initial gas concentration , U_g is superficial gas velocity, Z is depth of the column, k_0 is constant. Equation (1-19) can be simplified to the following general form:

$$C_o - C = K_0 t \tag{1-20}$$

where $K_0 = A\ k_0\ \delta$, and time, $t = z/U_g$. Equation (1-20) is similar to a zeroth-order kinetic equation generally used in biochemistry, which is typically written as $C = C_o - k_o t$.

Reaction and diffusion limitation

For reaction and diffusion limitations, the second BC for the equation (1-5) as given in equation (1-7) is now changed to the following equations:

$$x = \lambda, \qquad \frac{dC_l}{dx} = 0 \tag{1-21}$$

where, λ is penetration thickness. By integrating equation (1-5) and applying the BC in equation (1-21), the solution of the differential equation (1-1) becomes:

$$\frac{C_l}{C_g/m} = 1 + \frac{1}{2}\frac{\phi^2}{C_g/C_{go}}\left[\sigma^2 - 2\sigma\frac{\lambda}{\delta}\right] \qquad (1\text{-}22)$$

Since $C_l = 0$ at $\sigma = \lambda/\delta$, penetration thickness, λ, can be calculated from equation (1-22):

$$\lambda = \sqrt{2\frac{D' C_g}{k\ m}}$$

From a gas-phase mass balance on the substrate, it now follows for the gas concentration at a height h of the filter bed:

$$-U_g \frac{{}_{g}}{dz} = N\ A_s = k\lambda A_s \qquad (1\text{-}23)$$

From equations (1-22) and (1-23), it follows for the exit gas concentration $C_{g\text{-}e}$ with the BCs, $h = 0$ and $C_g = C_{go}$, that:

$$\frac{C_{g\text{-}e}}{C_{go}} = 1 - \frac{A_s\ Z}{U_g}\sqrt{\frac{k\ D'}{2\,C_{go}\ m}} \qquad (1\text{-}24a)$$

or,

$$\frac{C_{g\text{-}e}}{C_{go}} = \left[1 - \frac{Z}{U_g}\sqrt{\frac{k\ D'\ a}{2C_{go}\ m\ \delta}}\right]^2 \qquad (1\text{-}24b)$$

where a is interfacial area per unit of volume. At dynamic equilibrium, A_s, k, D', a and m are constants, and therefore Equations (1-24a) and (1-24b) can be written as the following

Equations (1-25a) and (1-25b), respectively.

$$\frac{C - C_o}{C_o^{\frac{1}{2}}} = Kt \qquad (1\text{-}25a)$$

$$\left(\frac{C}{C_o}\right)^{\frac{1}{2}} - 1 = -Kt \qquad (1\text{-}25b)$$

where

$$K = A_s\left[\frac{kD'}{2m}\right]^{\frac{1}{2}}$$

or

$$K = \left[\frac{k\,D'\,a}{2\,m\,\delta}\right]^{\frac{1}{2}}$$

and

$$t = \frac{z}{U_g}$$

First-order Reaction Rate

Ergas et al. (1993) developed an equation similar to that described by Ottengraf (1986). In the differential expression represented by equation (1-1), they believed that the reaction rate, R is not constant. Instead, they assumed that R follows first order kinetics as described by equation (1-4). The solution of the differential equation (1-1) with BCs from equations (1-6) and (1-7), and applying the gas-phase mass balance equation (1-23) in this case becomes

$$\ln\frac{C}{C_o} = -\frac{kA_sL}{HU_g}.\frac{\tanh\theta}{\theta}.z \qquad (1\text{-}26)$$

where C is the effluent pollutant concentration, C_o is inlet pollutant concentration, k is the first order rate constant, A_s is the surface area per unit volume of porous media, L is the biofilm thickness, H is Henry's law coefficient or m, Ug is the gas velocity through the column, θ is the Thiele number and z is the axial position within the filter column. Again, at dynamic equilibrium, A_s, L, H and θ are constant, and therefore equation (1-26) can be written in the following form:

$$\ln\frac{C}{C_o} = -K_1t \qquad (1\text{-}27)$$

Equation (1-27) is similar to the general form for a first order kinetic equation,

$$C = C_o \exp(-k_1t).$$

Summary

Biofiltration has been employed for many years to eliminate volatile inorganic and organic compounds from waste gases. The application of this technology has been widespread in European countries, particularly in Germany and The Netherlands. Even though biofilters were originally used for elimination of odorous gases, such as those from rendering plants, the possibilities for other applications have been shown to produce promising results. One of the applications that has provided positive results was the elimination of volatile organic compounds (VOCs).

Volatile organic compounds (VOCs) have been considered important by regulators if they are either precursors of photochemically produced ozone in the troposphere or species that are known to be potential carcinogens or toxic to human or animal species. For these reasons, increasingly stringent regulation of VOCs emissions is taking place, particularly in urban areas, where substantial levels of emissions of VOCs (> 10 ton/year) into the ambient air must be avoided.

Some VOC emission streams that contain low concentrations (< 1000 ppm) of organic compounds cannot be justifiably controlled by conventional air pollution control (APC) devices on a technical or economical basis. Biofilters provide an alternative APC technology which could be appropriate for treatment of low concentration gas streams containing VOCs, due to the nature of the process. Because biofiltration is a process that includes absorption and microbial transformation, its usefulness cannot be universally applied for all types of pollutants at the same operating conditions. Individual studies should be conducted on specific compounds in order to optimize the operation of the biofilter for elimination of that compound.

Butane, or n-butane, is a light straight chain aliphatic hydrocarbon that is produced commercially and used abundantly. Even though butane is not listed as an air toxic in Title III of the 1990 Amendments to the Clean Air Act, its involvement as a precursor of tropospheric ozone formation is the primary consideration for its destruction prior to discharge of waste gases to the ambient air. Health effects studies have been conducted to evaluate exposure to butane, but most of these studies were carried out on animals, for target organ evaluation. Unlike butane, benzene is a stable compound due to its unique structure. Benzene is not a photochemically reactive specie but its effects on human health are of primary concern. As a potential carcinogenic compound, it is included in the air toxics list in Title III, 1990 Amendments to the Clean Air Act.

Both butane and benzene are discharged from work areas to the ambient air, usually at low concentrations. Biofiltration appears to be the most suitable technology for treatment of these types of discharges. Technical evaluations of the elimination of butane or benzene using a compost biofilter have not been reported. Butane is one of the simplest straight chain hydrocarbons that might be readily transformed by microorganisms to less harmful species. However, the initial process in biofiltration, which involves absorption in an aqueous film, could be the rate limiting process for elimination of butane due to its low solubility in water. Benzene on the other hand, presumably because of its structure, is more difficult to transform using microorganisms. However, the latter compound does have a higher solubility in water than butane, which may increase its potential for elimination by biofiltration. Thus, in order to prove these hypotheses, intensive studies of the elimination of butane and benzene by biofiltration should be conducted.

CHAPTER 2
MATERIALS, EQUIPMENT AND OPERATION

Filter Materials

Filter materials used for biofiltration in this study were found from different sources: compost from Gainesville composting company, compost from Kanapaha waste water treatment plant, compost provided by Agricultural Engineering Department composting experimental plot and gasoline contaminating soil from Jacksonville .

Physical Analyses

Physical analyses of filter media included measurements of water content, pH, bulk density, particle density, porosity, temperature and pressure drops.

Water content

Water content of filter media was determined before the filter media was packed in the biofilter column and at other times during operation whenever necessary. Three locations along the column enabled access to the compost for media sampling (extraction) and water content determinations of used compost. Three to five grams of wet compost were weighed and dried in an aluminum tray at an oven temperature of 70°C until constant weight was obtained. Compost water content was determined by the difference in weight between the wet and dry compost samples (Robarge and Fernandez, 1986).

Organic matter

Organic matter content of the filter media was measured by a combustion method. The measurements were conducted at the start of the experiments and at certain times during biofilter operation. Following determination of water content, the dried samples were placed in a muffle furnace and combusted for 24 hours at 450°C. Organic matter was determined by the weight loss on ignition (Robarge and Fernandez, 1986).

Acidity of filter medium

Measurements of filter medium acidity were performed on a regular basis. Most of the time, the acidity measurements used the eluate from the filter media that drained to the bottom of the columns. Alternatively, at other times, compost samples were taken from 3 ports along the column and each of the samples was weighed and mixed with D.I. water in a liquid/solid ratio of 10 : 1 (Robarge and Fernandez, 1986). The wetted sample was shaken for 30 minutes and pH of the solution was measured by a calibrated pH meter (Corning Model M245) with an accuracy of ± 0.01 pH units.

Bulk density

Bulk density of the filter medium was measured before the biofilter was packed. The method used was based on that described by Blake and Hartge (1986b).

Particle density

A picnometer was used to measure particle density of the filter media. The procedure followed that described by Blake and Hartge (1986a).

Porosity

Porosity was calculated from measurement of the bulk density and particle density of the filter medium according to Danielson and Sutherland (1986).

Temperature

Temperature along the column was measured directly using mercury in glass thermometers with 0.2°C divisions. Temperature measurements were made at three locations along the column and the average and variation of temperature along the column could be determined.

Particle size distribution

Particle size distributions by weight were measured by passing the compost through a series of sieves (U.S.A. Standard Testing Sieve, A.S.T.M. E-11 Specification, Fischer Scientific Company). The compost from each size category was weighed and the weight was then adjusted to a dry weight basis.

Chemical Analyses

Four chemical parameters of the compost were determined chemically. These were nitrogen, carbon, phosphorous and organic content.

Nitrogen

Total nitrogen was analyzed using the Total Kjeldahl Nitrogen (TKN) test (APHA, 1989). First, a known amount of sample (0.2-0.5 g dried oven sample) was mixed with 20 mL D.I. water and stirred. Five milliliters (5 mL) Total Kjeldahl Nitrogen (TKN) mixture was added to the solution. The prepared sample was then digested in a digestor until a clear solution was obtained. After digestion, a distillation procedure was performed followed by titration with standard 0.02N H_2SO_4 titrant until indicator turned a pale lavender. Indicator solution was made of dissolved 200 mg methyl red indicator in 100 mL 95% ethyl alcohol and dissolved 100 mg methylene blue in 50 mL 95% ethyl alcohol. Five drops of this mixed indicator solution was added to the digested sample before titration was performed. Ammonium content was determined in a similar fashion to that for total nitrogen content except that no digestion was performed. Total nitrogen was also analyzed using a Carlo Erba Model NA 1500 CNS analyzer and the result was used to determine C/N ratio of filter materials.

Total Carbon

Finely ground, oven dried compost sample (<100 mesh) was analyzed for total carbon using Carlo Erba Model NA 1500 CNS analyzer.

Water soluble phosphorous (WSP)

A known amount of wet compost (2 g dry weight equivalent) was weighed and put into a 50 mL centrifuge tube. D.I. water was added to the tube to obtain a compost to liquid ratio of 1 : 10 on a dry weight basis. This sample was allowed to agitate for about one hour. The compost suspension was then centrifuged at 6000 rpm for 15 minutes and the solution filtered through a Gelman 0.45 micrometer membrane filter. The filtered solution was acidified ($pH < 2.0$) with one drop of concentrated H_2SO_4 and stored at 4°C until analyzed. The soluble reactive P (SRP) in the filter extract was determined colorimetrically (APHA, 1989) using a spectrophotometer (Shimadzu UV-160) with 1 cm path length at 880 nm wavelength.

Table 2-1. Properties of composts used in the biofilter column experiments.

Properties of filter media	Filter Medium No:*							
	1	2	3	4	5	6	7	8
TKN, % NH_4-N	0.305	0.506	0.209	0.89	1.32	1.21	0.98	1.11
NH4, % NH_4-N	0.060	0.110	0.045	0.048	0.22	0.18	0.16	0.11
P, % PO_4-P	0.0015	0.0035	0.001	0.004	0.0044	0.0049	0.0038	0.005
Total C, wt%	36.8	45.1	0.335	5.834	32.312	41.26	44.15	38.65
Total N, wt% (CNS analyzer)	0.998	1.894	0.190	0.800	1.038	1.063	0.88	1.13
C/N	36.8	23.82	1.76	7.30	31.13	38.81	50.17	34.2
Particle density, $g.cm^{-3}$	1.90	1.70	2.90	2.23	2.21	1.90	1.64	1.70
Bulk density, $g.cm^{-3}$	0.578	0.566	0.95	0.89	0.70	0.54	0.41	0.70
Porosity, %P	69.6	66.7	67.2	64.1	68.3	71.6	75.0	58.8
Organic content, $g.g^{-1}$ (db)	0.724	0.901	0.35	0.6	0.78	0.73	0.65	0.74
pH	7.5	8.0	7.8	7.5	7.0	7.2	7.2	7.1
Water content, % (wb)	60	80	30	44	60	62	65	64
Median particle size, mm	3.5	2.5	0.66	0.8	1.18	2.1	4.7	3.0

* 1. Compost found from Gainesville composting company and used in bench scale column 1 for butane removal.
2. Compost found from Kanapaha waste water treatment and used in bench scale column 2 for butane and benzene removal.
3. Gasoline contaminating soil from Jacksonville and used in column 1 of small column biofilter for butane removal.
4. Mixture of material number 3 and < 3 mm size compost from Gainesville, used in small column 2 for butane removal.
5. < 3 mm size compost from Gainesville and used in small column 3 used for butane removal.
6. 3-5 mm size compost from Gainesville and used in small column 4 for butane removal.
7. 5-12 mm size compost from Gainesville and used in small column 5 for butane removal.
8. Compost found from Agric. Eng. exp. plot and used for benzene removal in 3-stage and bench scale column 1.

Total phosphorous

Ground and oven dried compost was weighed (≈ 0.05 g), mixed with 50 mL D.I. water and stirred. One milliliter of strong acid HNO_3 was added to this mixture in a 125 mL Erlenmeyer flask. Boiling beads were added to the mixture and it was then boiled until about 10 mL of solution remained. One drop phenolphthalein was added and the color adjusted with NaOH solution to a faint pink solution. The solution was brought back to colorless by adding strong acid solution dropwise and then allowed to cool down. After cooling, 2 mL of ammonium molybdate reagent was added and the solution diluted to 50 mL with D.I. water. Five drops of stannous chloride were added to the solution and the solution was mixed. Then, the mixture was allowed to incubate in a dark room for about 10-12 minutes. Finally, the color intensity of the solution was measured using a spectrophotometer at 690 nm (APHA, 1989).

Microbial Activity Analyses

Bacterial activity inside the compost used for butane removal was measured using the dehydrogenase method. Biological oxidation of organic compounds is generally a dehydrogenation process. The overall process for dehydrogenation may be represented as follows:

$$XH_2 + A \rightarrow X + AH_2$$

where, XH_2 is an organic compound (hydrogen donor) and A is the hydrogen acceptor.

A modified version of the dehydrogenase method described by Lee et al. (1988) was selected for use. First, the compost sample, about 1 g dry basis, was weighed and extracted using about 50 mL of tris-hydroxymethylaminomethane (TRIS) buffer solution. The solution was filtered to obtain the substrate sample. The pH of the substrate was adjusted to about 7.6 with 20% HCl because the optimum reaction of 2-(p-iodophenyl-3-(p-nitrophenyl)-5-phenyltetrazolium chloride (INT) occurs at this pH. To a 5 mL sample of near neutral substrate solution was added 0.5 mL of 3.95 mM (0.2 % wt) of INT. The mixture was incubated in the dark for about 20 minutes, then the solution was agitated for mixing purposes. To stop the reaction, 0.5 mL of 37 % formaldehyde was added to the mixture. Two mL of quenched reaction mixture was centrifuged at 1500 x g for 10 minutes. After centrifugation, the supernatant was decanted and 5 mL of dimethyl sulfoxide (DMSO) was added.

Vortexing the solution for 15 seconds followed, to resuspend the pellet, and the solution was incubated in darkness for 15 minutes to allow extraction of INT formazan (INTF). Finally, the extract was clarified by centrifugation (1500 x g for 10 minutes) and the optical density of the supernatant was analyzed by absorption spectrophotometry at 640 nm.

Blanks containing autoclaved samples, were included in the procedure for control purposes. Standard solutions for INTF were prepared at 0.5, 1, 1.5, 2.0, 2.5, and 3 x 10^{-5} mole/L in DMSO for calibration purposes.

Equipment and Operation

Four different operating scales of biofilter systems were constructed for the proposed experiments. The first system, consisting of two similar columns, were used to treat both butane and benzene and was designated as a bench scale biofilter. The second system consisted of 10 small columns arranged with duplicates filled with five different types/sizes of filter media (filter materials # 3, 4, 5, 6 and 7 of Table 2-1), which was used to eliminate butane and it was referred to as the small-scale biofilter system. The third system consisted of three columns, which was used to treat contaminated air containing benzene injected in the air stream by a syringe pump and was called a three-stage column. The fourth one was a batch system, which was used to study the effects of inlet benzene concentrations, water contents, temperatures and different pH on benzene removal.

Bench-Scale Biofilter System

Design and construction

The design of the bench-scale biofilter employed in this study was similar to that described by Yang (1992). A schematic drawing of the bench-scale column biofilter is shown in Figure 2-1. The system basically consisted of a gaseous pollutant dilution system, an air blower, a prehumidification column, two biofilter columns and the venting system.

Before entering the humidification column, pure butane gas was first diluted with a filtered laboratory air supply using a two stage dilution system which included dead volume flasks to stabilize and adjust the flow rate of the pollutant mixture. A schematic diagram showing the butane dilution system is presented in Figure 2-2. In the case of benzene, the pollutant introduction system to the column was different to that for butane. Because benzene used in this study is normally in the liquid form, evaporation of benzene in air before dilution was necessary.

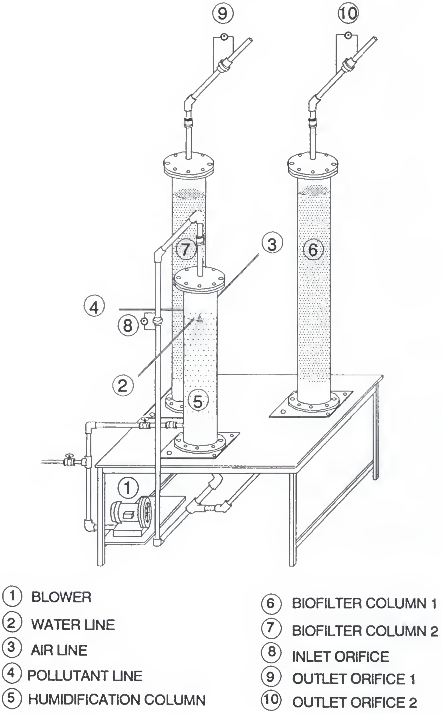


Figure 2-1. Schematic drawing of bench-scale biofilter system..

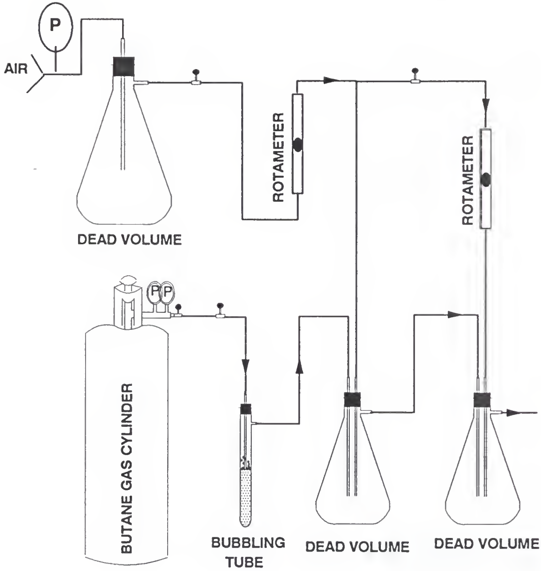


Figure 2-2. Schematic drawing showing the butane dilution system.

A schematic diagram of the evaporation and dilution system for benzene is presented in Figure 2-3. A heating jacket with a heat controller was installed to provide for rapid benzene evaporation. Liquid benzene was placed in a glass bottle which was fitted with inlet and outlet ports as well as a port for filling with benzene. The inlet port of the evaporation bottle was connected to an air line from a compressed air tank. In this line was a needle valve, an orifice made from a syringe needle and a rotameter. A needle valve was used to control the air flow into the evaporation bottle, the orifice was used to regulate the incoming air flow, and a calibrated rotameter was employed to measure the air flow rate. By adjusting the air flow rate into the evaporation bottle and the heat controller, the concentration of benzene in a known flow of incoming air could be estimated. However, in order to precisely measure the concentration of benzene, samples of the benzene-air mixture were injected to the GC-FID.

The two biofilter columns, identified as column number 1 and column number 2, could be run simultaneously and controlled separately. Each column was built from 15 cm (inside diameter) and 140 cm (length) of clear acrylic pipe. Both columns were filled with the desired filter medium up to 120 cm height. At about 10 cm from the bottom of the column, a-15 cm diameter sieve, made of acrylic plate, was placed to allow the gas stream to distribute equally across the face of the column and to support the filter media bed. Glass fiber was placed on the top of the sieve in order to prevent small size particles of filter media from penetrating to the bottom of the acrylic column. The filter media (compost) was packed inside the column on the top of the glass fiber up to the desired height.

Nine sampling ports along each column were provided for gas sampling purposes.

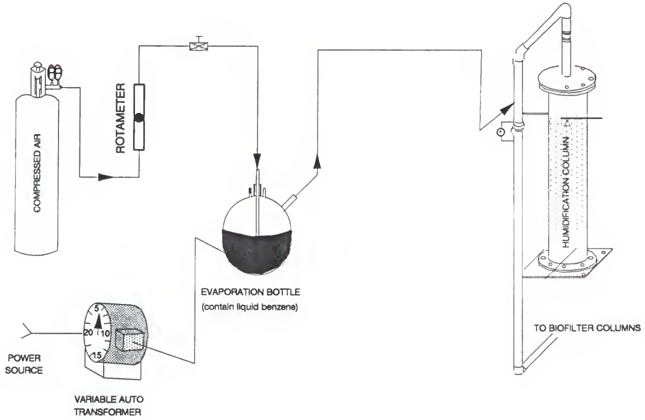


Figure 2-3. Schematic diagram for evaporation and dilution system for benzene in the bench-scale column.

Three additional ports were constructed near to the central gas sampling ports for temperature measurements. Three larger ports were also placed on the opposite side of the columns to the gas sampling ports for compost/filter medium sampling purposes. Two other ports, which were located at the inlet and outlet of the filter bed were included for pressure drop measurements by connecting the latter ports to the opposite legs of a water manometer. Schematic diagrams of the configuration of sampling and measurement ports are presented in Figures 2-4 and 2-5.

The carrier gas flow rate from an air blower (Gast Regenair Model R 3105-1) was controlled by a rotary valve installed at the inlet to the humidification column. The flow rate was then measured by a calibrated orifice meter installed at the outlet of the humidification column. Total flow rates of the pollutant and air were rechecked by measuring the outlet flowthe outlet flow rate of each biofilter column using calibrated orifice meters.

Operational procedures

Room air was forced by a Gast Regenair Model R 3105-1 air blower into the humidification column. The blower was driven by an half horse power (HP) motor which generated a maximum flow of 1.5 $m^3.min^{-1}$ and a maximum pressure/vacuum of 11/10 kPa (1100/1000 mm H_2O of water column). Humidification of the incoming air was achieved by atomizing water in the chamber through a nozzle, as the room air passed. To improve the humidification of inlet air, Pall rings were stacked under the water spray to increase surface area for contacting the inlet air with liquid water.

n-Butane (Specialty Gas; 99% purity), stored in liquid phase in the gas cylinder, was continuously vented. The butane gas was directed to the humidification column where it was

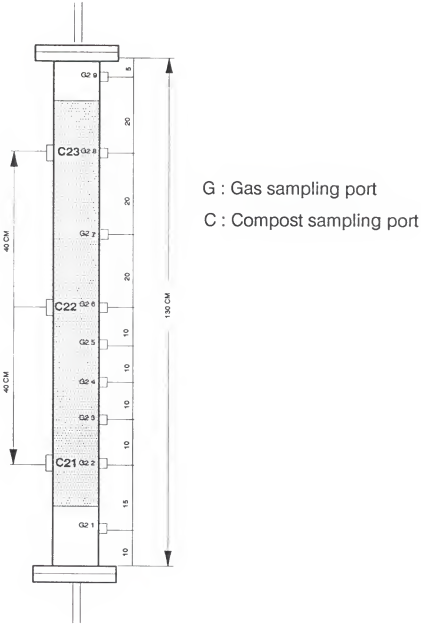


Figure 2-4. Schematic diagram of gas and compost sampling ports for bench scale column.

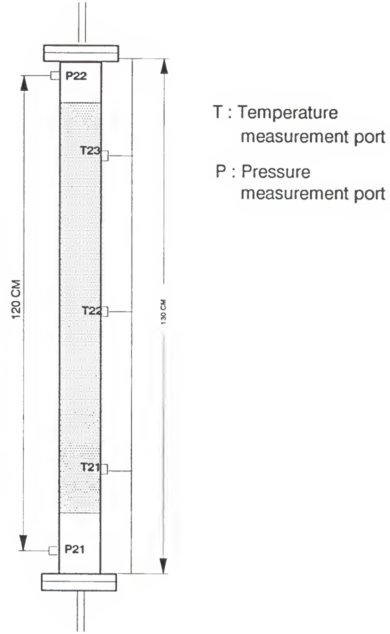

P22
T23
T22
T21
P21
120 CM
130 CM
T : Temperature measurement port
P : Pressure measurement port

Figure 2-5. Schematic diagram of temperature and pressure measuring ports for bench scale column.

diluted with room air generated from the air blower. Pre-dilution of butane with air was carried out just before it was vented into the humidification column. Contacting the gas being treated with the water spray resulted in better mixing between the pollutant gas and humidified air. Flow rates of air were controlled by the rotary valve, which was installed at the inlet of the humidification column. The total inlet flow rate (air + pollutant) was measured by an orifice meter installed between the outlet of the humidification column and the inlets to the biofilter columns.

Butane flow rate from the gas cylinder was detected by bubbling the gas into a glass trap containing water. The air flow rate for pre-dilution of butane was controlled by a pressure gauge valve and needle valve, and was measured by a calibrated rotameter. In the case of benzene, benzene vapor generated from a heated flask containing liquid benzene was mixed with cylider compressed air, and the flow rate of benzene air mixture was measured by a calibrated rotameter. On/off valves were installed at the inlet and outlet of each biofilter column to facilitate shutting down operation of either column for repair, maintenance or calibration if necessary, while the other column was still in operation. The outlet flow rates from each column were measured using calibrated orifice meters installed at the column outlets to ensure that inlet and outlet flows were similar, otherwise gas leaks might be present along the system. A small port fitted with a liquid spray outlet was installed on the top of each biofilter column for introduction of additional water, nutrients or other necessary reagent solutions if needed.

Gas sampling procedures

The pollutants were sampled from the continuously operating biofilter system using

Tedlar bags on the average every 2 (two) days during the filter conditioning period. Gas sampling was carried out at the inlet and outlet ports of each column. After the biofilter reactors had achieved stable operation, sampling was routinely performed at the other seven ports located between the inlet and outlet ports of each column. By simultaneously sampling the polluted air through the nine ports along the column, the elimination capacity along the biofilter column could be easily and accurately determined. Also, the kinetics of the pollutant elimination process could be studied based on the distance from the inlet at which the sample was taken.

Gas sampling through the ports was carried out using permanently placed gas probe made of Teflon tubing with small holes bored along the length of the probe, which were perpendicular to and faced the direction of the gas flow. The purpose of these small openings in the gas probe was to obtain representative samples of the gas profile flowing through the column. The outlet of the gas probe was connected to Tygon tubing equipped with a clamp in order to easily open and close the outlet for sampling purposes. The outlet of the Tygon tubing was attached to a Tedlar bag when sampling was carried out.

Each port was equipped with a gas sampling probe so that the probe always stayed in the same position in the biofilter. The advantage of using a fixed gas probe at each port was to avoid the effects of contamination when different concentrations were sampled at different ports. In addition, it could avoid problems in disturbing the biofilter bed and identically relocating the probe position at each port. Also, using a permanent separate probe for each port avoided the necessity of frequently opening and closing the ports, so that exposure to pollutants could be eliminated. Frequent opening and closing of the ports for sampling purposes could also increase the leakage of pollutant to the room air (laboratory) which could affect room air background levels of pollutants.

Sampling of the waste gas stream on each column was usually performed at the same time at all gas measurement ports. The Tygon tubing line was vented for 15 seconds then a collapsed, cleaned Tedlar bag with the port number marked on it was connected to the sampling port through the Tygon tubing outlet from the probe. Then, the bag valve was opened from one half to one full turn depending on the size of the bag and collection time. The clamp used to close the port outlet on the Tygon tubing was removed and the waste gas was allowed to flow into the sampling bag. When sufficient gas sample (≈1 L) was collected in the bag, the clamp was replaced on the Tygon and the bag valve was closed up. The sampling time used to collect samples from all 9 ports along the column varied from 5 to 30 minutes depending upon the sample gas flow rate, water content of filter medium and the extent of the bag valve opening.

When the pollutant samples along the column had been collected in the sampling bags, the pollutant content was then determined using a commercial (Varian Model 3700) gas chromatograph-flame ionization detector (GC-FID) method. Following analyses of samples by the GC-FID analyzer, the sample bag was flushed using purified nitrogen gas (N_2) until the bag was found to be clean (undetectable pollutant by GC-FID). Usually, from two to five flushings of each bag with N_2 was necessary to clean the sample bags. A schematic diagram showing the procedures for gas sampling and analysis is presented in Figure 2-6.

Gas measurements and analyses

Bulk gas measurements consisted of monitoring volumetric flow of the air stream

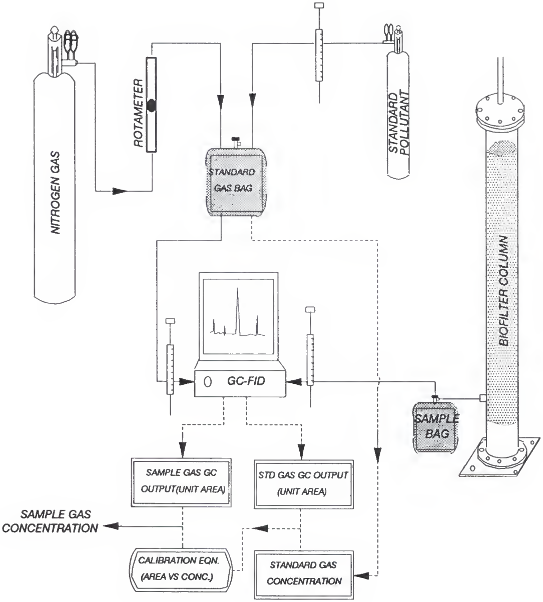

NITROGEN GAS
ROTAMETER
STANDARD GAS BAG
STANDARD POLLUTANT
BIOFILTER COLUMN
GC-FID
SAMPLE BAG
SAMPLE GAS GC OUTPUT(UNIT AREA)
STD GAS GC OUTPUT (UNIT AREA)
SAMPLE GAS CONCENTRATION
CALIBRATION EQN. (AREA VS CONC.)
STANDARD GAS CONCENTRATION

Figure 2-6. Schematic diagram of gas sampling and analyses method for bench-scale column studies.

passing through the biofilter column. Gas analyses were used to quantify the pollutant concentrations in the air stream as it passed along the column. In order to quantify the pollutant concentrations, multipoint pollutant gas calibration checks were performed routinely prior to and subsequent to gas sample analyses.

The flowrate of the contaminated air stream through the biofilter system was measured using calibrated orifice meters. Three orifice meters were installed in the bench-scale biofilter system. The first orifice meter was installed at the outlet of the humidification column leading to the biofilter column inlets. The other two orifice meters were installed separately at the outlets of the two biofilter columns.

Calibrations of the three orifice meters were carried out prior to initial biofilter operation and were checked on a regular basis. Calibration were carried out using a wet test meter whose meter constant was known. The inlet orifice meter measured the total flow rate of the gas stream entering the biofilter columns. The two outlet orifice meters measured the total flow rate of gas leaving the individual column biofilters. Differential pressure (ΔP) measurements across each of the orifice meters were used to indicate the flow rate of gas passing the orifice. Differential pressure values were converted to the flow rate (standard liter.min^{-1}) from the calibration curve or derived calibration equation after corrections for system pressure drop. The flow rate at the biofilters inlet, as measured by the inlet orifice meter, should be the same as the sum of the flow rates measured by the two outlet orifice meters. The overall flow rate of gas was adjusted by a rotary valve, which was located at the inlet of the humidification column.

A Varian model 3700 gas chromatograph (GC) equipped with a 30 m DB-5 wall coated open tubular column and flame ionization detector (FID) was used to measure concentrations of hydrocarbon in this study. Before any samples were analyzed by GC-FID, the analyzer was calibrated for target compounds. In the case of butane, standard calibration mixtures were made by diluting a known (certified) concentration of butane (10,000 ppm) to specific concentrations. Several standard butane concentrations were prepared by sequential dilution of the 10,000 ppm butane standard with nitrogen gas. In the case of benzene, standard calibration mixtures were made by diluting known quantities (syringe samples) of liquid benzene to specific concentrations using a dilution bottle containing nitrogen gas and heated to about 100°C for about one hour to evaporate the liquid benzene.

Prior to standardization of the GC, the GC carrier gas flow rate, air and hydrogen to the flame were optimized. Seven syringe injections were made for each standard concentration mixture. The mean value and standard deviation of peak area for each standard concentration of butane was calculated. A linear regression analysis provided an equation and graphical representation for the specific mass range of operation. The quantity of butane in real samples were derived from the peak area versus mass standard relation or interpolated from the corresponding graph.

Sample analyses involved, at least two calibration standard checks to assure the quality of the data obtained. These standards were checked for retention time and peak area reproducibility to assure that the analytical estimation was performing within appropriate working limits (± 2 std deviation) of the mean control value. The operating conditions of the GC-FID used in this study are given in Table 2-2.

Table 2-2. Varian model 3700 GC/FID operating conditions.

Parameters	Values	
	Butane	Benzene
Temperatures: °C		
- Injection port	150	200
- GC column	50	50
- Detector	200	250
Flow rate, mL.min.$^{-1}$		
- Carrier gas (Helium)	35	6.5
- Air	300	300
- Hydrogen gas	30	30
Retention time for hydrocarbon, min.	0.4	4.0
Detection limit for hydrocarbon, ppm	0.2	0.2
Attenuation of GC, amps.mv^{-1}	10^{-10}	10^{-11}

Routine gas analyses

Gas samples were taken every two days during biofilter operation from the inlet and outlet gas ports of the column using Tedlar bags. The gas sample in the bag was extracted and injected directly to the GC-FID using a one milliliter gas tight syringe. The volume of sample injected to the GC was mostly 0.75 mL. Quantification of the concentration of sample gas was done by converting it to part per million (ppm) from the calibration standard curve. To check that the GC-FID was operating correctly, two or three known concentrations of standard gas were prepared and injected into the GC-FID every time a series of analyses were carried out. These calibration check values were used to adjust or confirm the existing standard calibration equation.

Small Scale Biofilter System

Design and construction

A small scale column biofilter system was constructed for studying the effects of different filter media (filter media # 3, 4, 5, 6 and 7 as given in Table 2-1) and other operational variables on butane removal. Figure 2-7 shows the layout of the small column biofilter system. This system consisted of 10 columns with a common manifold for introduction of different test gases into the columns. The columns were made from glass pipes with an inside diameter (ID) of 50 mm and 300 mm length each. These columns had an effective packing height of about 250 mm, which provided approximately 490 mL packed volume.

A calibrated rotameter was situated upstream of the manifold to measure the flow of

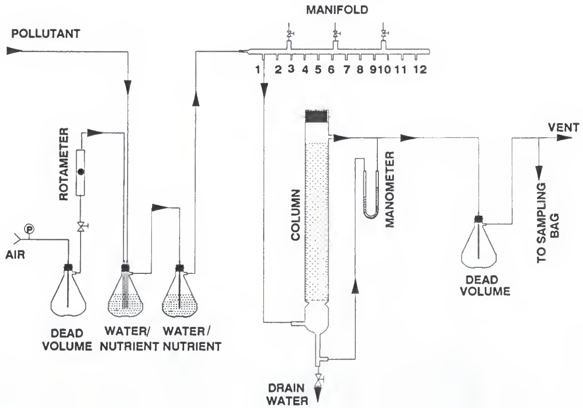


Figure 2-7. Schematic diagram of small scale biofilter systems.

the air stream containing pollutant. Syringe needles, all of the same diameter, were installed at the outlets of the manifold to distribute the gas stream equally into 10 columns. Both the air and pollutant gas were prehumidified by bubbling the gases through water traps installed prior to the manifold to maintain moisture in the filter media.

Empty flasks were connected to the outlet lines of the columns to stabilize the flow through the system and to drain excess water. Also, an empty flask was installed prior to the inlet rotameter to dampen rapid flow variation from the pump and drain water drops from the humidified gas. The stabilized flow was measured by a rotameter. The sampling of inlet gas was conducted at one of the inlet manifold outlets whereas sampling of outlet gas concentrations were performed at the column outlet following the damping flasks. Gas samples were taken using Tedlar bags.

Operational procedures

Laboratory air was blown through a flask using a pressure regulator for gas flow control. The air then flowed through a needle valve to regulate the air flow, which was measured with a calibrated rotameter. Following flow measurement, the air flow passed through Teflon tubing to a mixing flask. Before the mixing flask, the air flow was regulated using another needle valve and measured using another calibrated rotameter. Air entering the mixing flask was mixed with .pollutant gas entering by a separate line. The gas mixture passed to a second flask which was either empty in some cases or contained water and inorganic nutrient. The purpose of the second flask was to stabilize the flow and to make available the possibility for watering and/ or adding nutrient to the filter media.

Following the second mixing flask, the gas stream was directed to a manifold where the gas mixture is distributed equally to 10 columns using identical syringe needles installed at the each outlet of the manifold. The component gas streams exit from each column through an outlet and flask. The latter was used to stabilize the flow prior to venting. Flow of the air (carrier gas) and pollutant could be adjusted by the in-line needle valve and measured by a calibrated rotameter. The pollutant (butane) gas flow was controlled by bubbling the gas through a water trap and adjusting a very fine needle valve at the inlet to the trap.

Gas sampling procedures

For small scale biofilter experiments, gas sampling was carried out using Tedlar bags, on the average every two days of operation. Inlet concentrations were sampled at the outlet of the manifold and the column outlet concentrations were measured at each column outlet. In the case of low flow rates for this small scale system, gas sampling was performed using a closed outlet procedure. The closed outlet procedure involved gas sampling by closing the outlet and allowing gas to flow directly into the sampling bag. However, to avoid the effect of pressure build-up along the system, sampling was stopped before the bag was completely filled with sample gas. Usually sampling was terminated before the sample occupied one half of the bag volume. On the other hand, if the flow of the gas through the system was high, gas sampling was performed using an open outlet procedure. The open outlet procedure involved sampling the gas through the gas outlet line while the column outlet was still connected to the vent. This sampling procedure avoided pressure build-up along the system and allowed for a longer sampling time.

Gas measurements and analyses

Gas measurements and analyses were carried out in a similar fashion to those described for the bench scale column biofilter.

Three-Stage Biofilter System

The design of the three-stage biofilter employed in this study consisted of three small packed columns connected vertically in series with an air space between each stage. A drawing of the three-stage column biofilter is shown in Figure 2-8. The experimental system essentially consisted of a syringe pump for introduction of benzene into the system line, an air blower, a prehumidification flask, the series biofilter column and vent system.

Benzene was injected by a syringe pump through a septum into the line, which was installed between the rotameter and empty flask. This empty flask provided a dead volume for mixing benzene vapor with air. Each column was built from 7.5 cm inside diameter and 40 cm total length of PVC pipe and was filled with the same type and amount of inoculated compost up to 30 cm height. The identical columns could be easily exchanged with each other or replaced by another column if required. At about 5 cm from the bottom of the first column, a 7.5 cm diameter sieve, made of acrylic plate, was placed to allow the gas stream to distribute equally across the face of the column and to support the filter media. A thin pad of glass fiber was placed on top of the sieve plate in order to prevent small size particles of filter media from penetrating to the bottom (inlet) of the column.

Seven sampling ports located along the length of the three-stage column were provided for gas sampling purposes. Three larger ports were incorporated, on the opposite

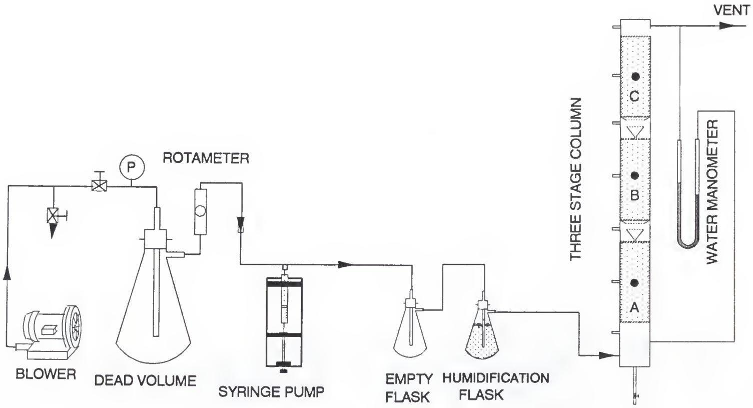


Figure 2-8. Schematic drawing of three-stage biofilter system.

side of the column to the gas sampling ports, for compost/filter medium sampling purposes. Two other ports, which were located at the inlet and outlet of the three-stage column were provided for pressure drop measurements. The latter ports were connected to the opposite legs of a water manometer. A detailed schematic diagram of the configuration of the sampling and measurement ports is presented in Figure 2-9. The flow of benzene from the syringe pump was adjusted by selecting the range and percent flow rate of the syringe pump.

The carrier gas (room air) flow rate, which was provided by an air blower, was controlled by a needle valve installed in the inlet line of the system. To stabilize the flow rate, a critical orifice made from a syringe needle was installed following the needle valve. The flow rate was then measured by a calibrated rotameter installed in the line prior to the syringe pump. A mercury manometer was installed prior to the rotameter to measure the pressure drop across the line for flow rate correction. An empty flask was installed directly after the syringe pump for mixing the benzene and vapor air, as well as for dumping the fluctuating gas flow. Another flask was installed after the empty flask to serve as a reservoir for humidifying water or nutrient solutions, if required.

Batch System Experiments

A comprehensive study of the effects of temperature, compost water content, compost acidity (pH), and initial benzene concentrations on benzene elimination was conducted in a batch system. Active compost from column 1 of a bench-scale system that had previously been used for elimination of benzene was selected as the medium for benzene elimination studies in the batch system. Unused or left-over compost that was used to construct the

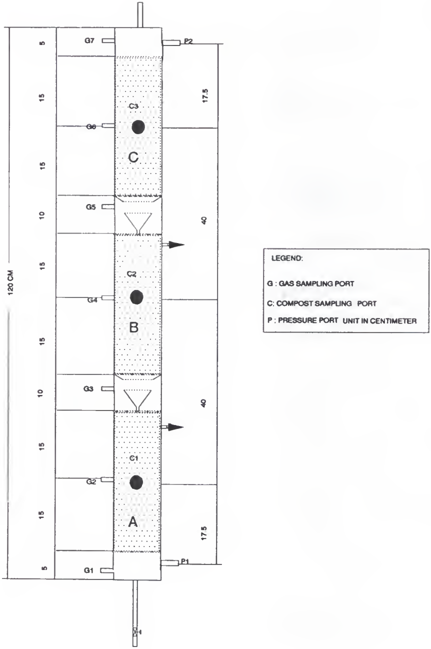


Figure 2-9. Schematic diagram of pressure drop, gas and compost sampling ports for three-stage biofilter.

biofilter in column 1 of the bench-scale system, was used as a control, after it was autoclaved for about one hour in order to sterilize inherent microorganisms.

Benzene vapor disappearance was examined in 160 mL glass bottles sealed with Teflon-faced silicon septa and aluminum crimp caps. Each bottle contained 15 g (dry basis) of compost at 20, 40, 60 and 80 % (wet basis) water contents. A combination of duplicate experiments under various conditions for three different compost pHs (3, 7 and 11), three different operational temperatures (5, 30 and 55°C), and two initial benzene concentrations (100 and 200 ppm) were set up for this study. pH was not included in the experimental variable combinations for the control compost, because it was presumed that biodegradation activities would be negligible and, therefore, compost pH would not affect the removal of benzene due to non-biodegradation. As a result, controlled experiments were reduced to three times less studies than the active compost experiments.

Glass bottles were autoclaved for one hour before they were filled with the compost. Compost water content was adjusted either by adding D.I. water to the compost or by gently drying the compost in a room air to meet the desired compost water content. The desired compost pH was achieved either by adding dilute hydrochloride acid or by adding dilute sodium hydroxide solution to obtain compost pHs of 3 or 11, respectively. For those compost samples with a pH of 7, however, the original compost was used because it was initially neutral (about pH 7).

Fifteen grams (dry basis) of compost sample, which had been conditioned to the desired water content and pH value was loaded into a 160 mL glass bottle with identifying number. The temperature selection for the experiments at 30 and 55 °C were made by heating a water bath with a stirrer and heater controlled by an automatic transformer, in which the experimental bottles were placed. To obtain a 5°C operational temperature, ice was added to cold water in a bath. A mercury-in-glass thermometer was employed to measure the water temperature in the bath.

A known concentration of benzene vapor was prepared in a 5 L Tedlar bag. Aliquots of this vapor were taken and injected using a millimeter gas tight syringe into sample bottles containing compost and air to obtain desired benzene concentrations. Initial samples for GC analysis were taken about 30 seconds after benzene vapor was loaded to the sample bottles. The GC analysis time for benzene was about 4 minutes. Samples for analyses were simultaneously taken from the group of twelve sample bottles every hour. This procedure allowed for analyses by GC-FID of the twelve samples at 5 minute intervals. Usually one group of experiment consisting of these sample 12 bottles was terminated after two to four hours, depending on the rate of benzene elimination in the head space sample.

Additional experiment on benzene elimination using duplicate compost bottle at neutral pH (pH=7), 30°C temperature and 60% water content was conducted in greater detail. Injection of head space sample from each bottle into the GC-FID were carried out at 10 minute intervals. These detailed studies were performed knowing that these conditions were the optimum for benzene elimination in the compost based on results from the previous batch system experiments. Five different initial benzene concentrations varying from about 34 to 866 ppm were used in this study.

CHAPTER 3
RESULTS AND DISCUSSION

Biofiltration of Butane

Biofilter systems, which consisted of two different scales were constructed for the proposed experiments on butane removal: bench-scale and small-scale column biofilters. The bench-scale system consisted of two similar columns filled with two different filter media (Compost # 1 and 2 as shown in Table 2.1, page 40). Both biofilter columns were treated in a similar way during the period of the experiments. The small-scale system consisted of 10 small columns arranged to provide duplicates filled with five different types/sizes of filter media .

The bench-scale biofilter system was constructed to study the total elimination capacity of butane. Moreover, the typical elimination capacity, temperatures, water contents, pressure drop and other physical and chemical properties of the compost along the column as well as microbial activities were investigated. The small-scale biofilter system was employed to study the effects of different types/sizes filter media on the removal of butane. Five different types/sizes of filter media (filter media # 3, 4, 5, 6 and 7 in Table 2-1, page 40) were used in this small-scale biofilter study.

Initial and long-term operations effects on the compost biofilter removal of butane will be reported and discussed in this chapter. Also, the kinetics of butane removal through the compost biofilter were determined. Statistical analyses using factorial design were used to compare the significant effects of different types of filter media and different inlet butane concentrations on butane removal.

Bench-scale Biofilter System

Initial biofilter operation

In the bench-scale biofilter system, Column 1 was loaded with a commercially produced yard waste compost from a Gainesville company (Compost # 1 in Table 2-1, page 40) and Column 2 was packed with a conventional yard waste compost found near Kanapaha waste water treatment plant (Compost # 2 of Table 2-1, page 40). The composts could be differentiated visually, where the Gainesville commercially produced compost consisted of a mixture of leaves, wood chips and sandy soil and the Kanapaha yard waste compost consisted mainly of wood chips. Detailed characterizations of these compost, which are given in Table 2-1 page 40, showed very little difference in their properties. Pressure drops across the packed columns were measured routinely. During long term operation, however, the pressure drop along the one meter column was only about 50 Pa (5 mm H_2O), because the flow rates used were low in order to obtain a long residence time. Both composts were inoculated with secondary activated sludge from Buckman waste water treatment plant in Jacksonville, Florida.

Maintaining water content of the composts in both columns was by humidifying the incoming gas/air stream. The humidification procedure proved to be good enough that the composts were found to retain a suitable water content without experiencing long-term drying. Even though the level of humidification for both composts was the same, the initial compost water content of Column 1 (about 60%) was less than that of Column 2 (about 80%). The difference in water content of these composts was not due to the difference in water content of the incoming air but was due to the difference in water holding capacity (WHC) of the composts used. From knowledge of the compost water holding capacity it may be deduced that the compost in Column 2 had a higher number of micropores than the compost in Column 1. WHC may be related to the surface area since the number of micropores is proportional to the surface area. Surface area is an important physical parameter for the compost in terms of biofiltration because the initial process in biofiltration is absorption, which is a function of available surface area.

Performance during long-term operation

The bench-scale biofilter system was operated continuously in 5 months. During the first 40 days of operation, the system could not reach a stable condition because of difficulties in achieving a suitable residence time. Also, the removal of butane through the biofilter is not as facile as removal of other higher molecular weight hydrocarbons even though n-butane is categorized as a light straight-chain aliphatic hydrocarbon, which presumably should be easy to be microbiologically oxidized (Hutzingen and Veerkamp, 1981). Kampbell et al. (1987) reported that the adaptation time for a soil bed filter in removal of a propellant mixture consisting of propane, isobutane and n-butane was about a month. Other biofiltration experiments, which were designed to remove hydrocarbons other than butane required about two weeks for the biofilters to achieve stable conditions (Ottengraf et al., 1984). As a result, the highest removal efficiency obtained during the first 40 days of operation was only about

75% with a residence time of 1 minute and inlet concentration of 25.5 ppm butane (see Figure 3-1). From these observations it was determined that the removal of butane through a biofilter required sufficient time for the hydrocarbons to be absorbed into the filter media and oxidized by microorganisms inside the biofilm, which was attached to the filter media. In subsequent studies, therefore, longer residence times were used, which were achieved by reducing the waste air flow rate to the biofilter.

After about 40 days of operation, air flow was continued through the biofilter but without introducing butane into the air stream, due to a leak found at the butane cylinder tank. Butane tank replacement was necessary and the system was run without butane for about two weeks. After butane tank replacement was carried out the system was operated again with longer residence times and lower butane inlet concentrations. After about 8 days of acclimation, the system reached stable operation as indicated by the high removal efficiency for Column 2 shown in Figure 3-1. During the latter operation, however, Column 1 continued to showed low removal efficiency. As explained earlier the compost in Column 1 presumably had a lower number of micropores, which is a property proportional to surface area, than did Column 2. The different surface area properties of the composts probably can explain why Column 2 always removed butane at a higher rate and efficiency than Column 1. Biofiltration involves two processes: absorption of pollutant into the biofilm, which is located at the surface of the filter medium, and oxidation of the pollutant in the biofilm by microorganisms. The first process, absorption, might be the dominant process for butane removal through biofilters. As a result, Column 2 which had more available surface area than Column 1, achieved a higher removal efficiency for butane. Figure 3-1 shows the

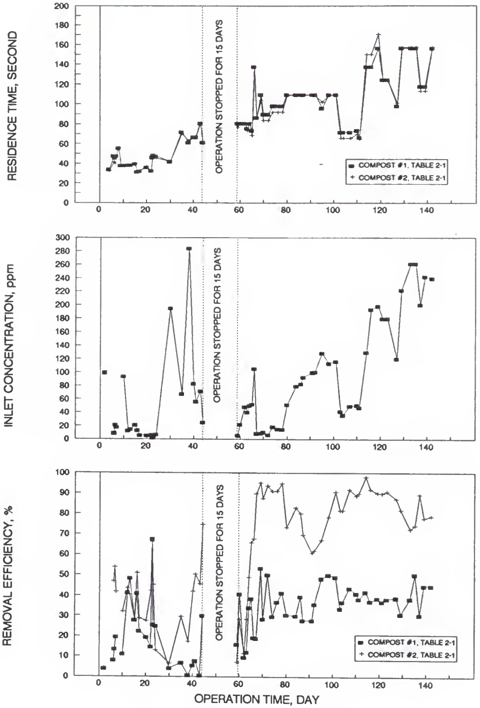


Figure 3-1. Profile of butane removal on continuous operation of a bench-scale biofilter system

relationship between removal efficiency, inlet concentration and residence times for the bench-scale biofilter system. As expected, the lower the inlet butane concentration, the higher the removal efficiency that was obtained. Also, the longer the residence time, the higher the removal efficiency that was observed. Low inlet butane concentrations resulted in complete absorption of pollutants into the biofilm and subsequent oxidation by microorganisms. Similarly, long residence times will allow the pollutant more time to be completely absorbed before finally being oxidized by existing microorganisms. The highest inlet butane concentration that could be removed at >90% efficiency by the compost biofilter in these experiments at the selected operating conditions was about 200 ppm with a residence time of 2 minutes. The water content was kept constant at the maximum water holding capacity for the compost. For the compost in Column 1, the water content was about 60% whereas in Column 2, it was about 80%. The acidity of the compost which was indicated by the pH value of the drained condensate was near neutral or slightly basic in both cases. The pH value for Compost 1 was about 6.8 and pH value for Compost 2 was about 7.25.

Microbial activities of the compost along the columns were analyzed using dehydrogenase assay as outlined in Chapter 2. The results of the calibration for iodo-nitrotetrazolium formazan (INTF) standard concentrations, the optimum value of optical density for those INTF standard concentrations and indicators of microbial activity in composts from the bench-scale columns are presented in Figures 3-2, 3-3 and 3-4, respectively. From these results, it is seen that microbial activities in Column 1 were relatively higher than those in Column 2. These results support the conclusion that the absorption mechanism, rather than microbial oxidation, is the rate limiting process for

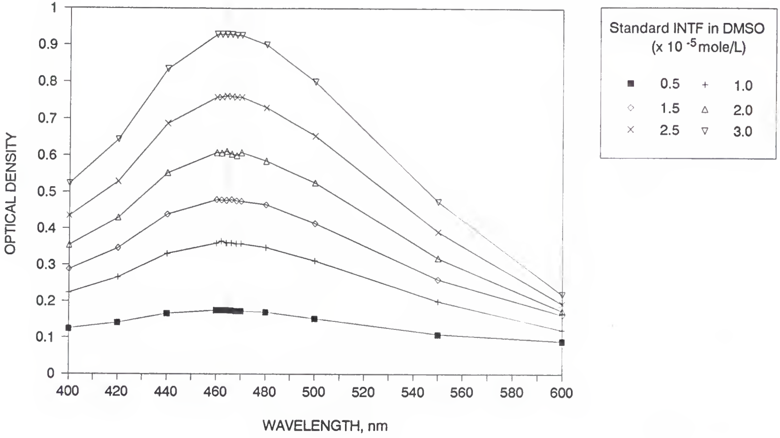


Figure 3-2. Calibration results for INTF standard concentrations.

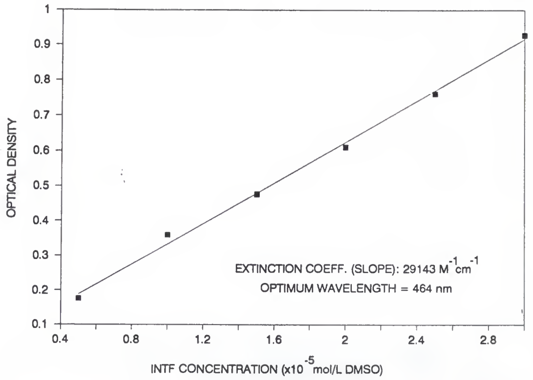


Figure 3-3. Maximum values of optical density of INTF standard concentrations used in the measurements of microbial activity.

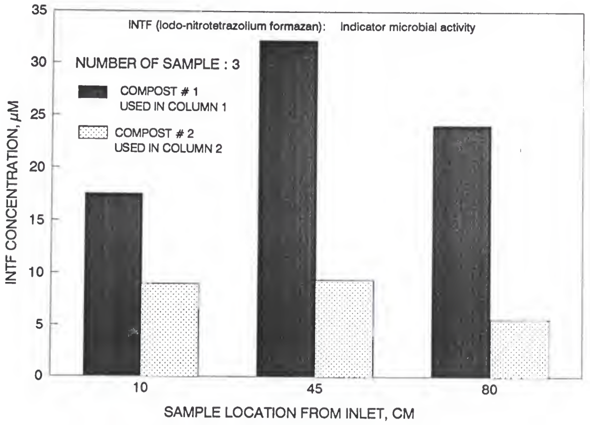


Figure 3-4. Indicators of microbial activity in sections of composts in the bench-scale columns.

removal of butane through the biofilter. Oxidation will occur whenever the pollutants are available in the biofilm, which is a result of the absorption process. The low absorption of butane into the biofilm layer is due not only to the low surface area of the filter media but also the nature of butane, which has a low solubility in water. Compounds like butane, which have low aqueous solubilities will be difficult to remove using biofilters not because of the difficulty in oxidizing them but because of the difficulty in absorbing these compounds into the aqueous phase biofilm before oxidation takes place.

Kinetics of butane elimination

Butane elimination rates along the columns of the bench-scale compost biofilter system were measured using all 9 sampling ports when the biofilter was operating at stable conditions. The profiles of butane elimination along the column were fitted to existing kinetic equations, which were developed specifically for biofiltration and were described previously in Chapter 1. Interestingly, from the data collected, the kinetic dependence of butane elimination through the compost biofilter did not appear to follow only one form of kinetic expression. Instead, elimination appeared to follow several of the kinetic relations depending on the inlet butane concentrations used. Figures 3-5, 3-6, 3-7, and 3-8 present examples of the kinetics of butane removal along Column 2 of the bench-scale biofilter system.

At low inlet concentrations (< 20 ppm), butane elimination along the column followed first order kinetics according to Equation (1-27), as presented in Figure 3-5. The regression formula could be expressed as $\ln(C/C_o) = 0.139 - 0.025\ t$ with a correlation coefficient squared, (R^2) of 0.975 and K_1 value of - 0.025 ppm.s^{-1} at an inlet concentration of 18.3 ppm.

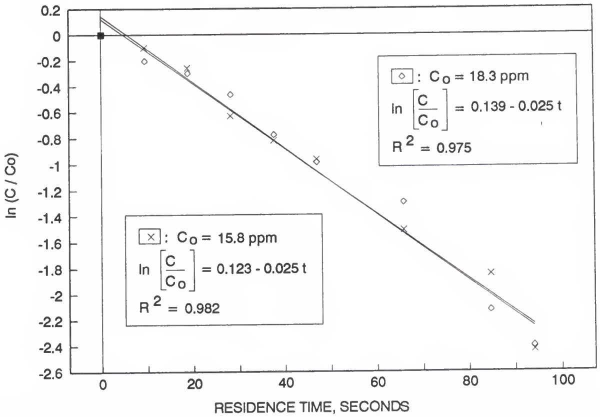


Figure 3-5. First-order kinetics of butane elimination on the bench-scale column.

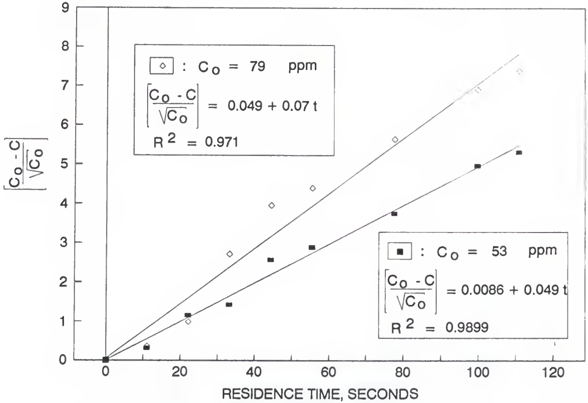


Figure 3-6. Intermediate order kinetics of butane elimination on the bench-scale column.

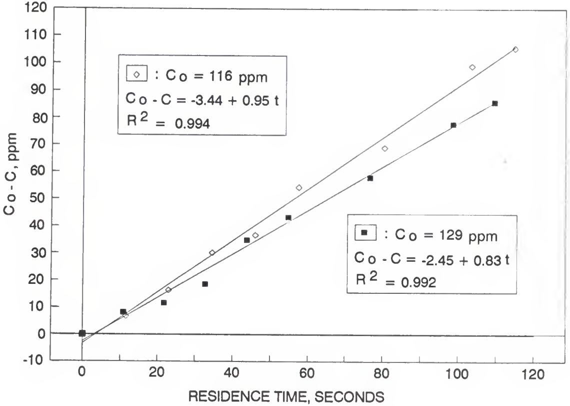


Figure 3-7. Zeroth- order kinetics of butane elimination on the bench-scale column.

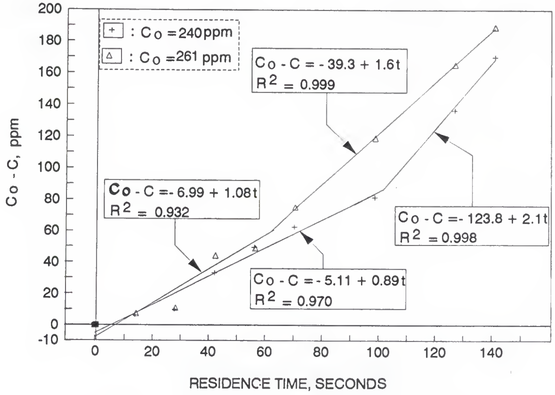


Figure 3-8. Double zeroth-order kinetics of butane elimination on the bench-scale column.

At higher butane concentrations in the range from 20 to 80 ppm, the data were fitted to Ottengraf's diffusion and reaction limitation model for zeroth-order kinetics as presented in equation 1-25. When the value of $(C_o\text{-}C)/\surd C_o$ was plotted against t, a straight line was obtained. At inlet concentration of 53 ppm and 79 ppm, as shown in Figure 3-6, the regression formulas are $(C_o\text{-}C)/\surd C_o = 0.0086 + 0.049\ t$ and $-(C_o\text{-}C)/\surd C_o = 0.049 + 0.07\ t$ with R^2 values of 0.9899 and 0.9709, respectively.

At inlet concentrations between 100 and 200 ppm, the data followed a relation describing reaction limitation of zeroth order kinetics, according to equation 1-20. Figure 3-7 is an example of this type of kinetic behavior. For inlet concentrations of 116 and 129 ppm for example, the zeroth order equations are $C_o - C = - 3.44 + 0.95\ t$ and $C_o - C = -2.45 + 0.83\ t$ with R^2 values of 0.994 and 0.992, respectively. K_0 values for these zeroth order reaction limitation relationships have units of $ppm.s^{-1}$. Therefore, these zeroth-order coefficients of 0.95 and 0.83 $ppm.s^{-1}$ correspond to maximum butane elimination capacities of 7.13 and 6.23 $g\text{-}butane.m^{-3}.h^{-1}$ for the compost in Column 2 at the operating conditions selected. It is noted that the specific gravity of butane is 2.085 $kg.m^{-3}$. Also, it should be pointed out that at an inlet concentration of 129 ppm, the elimination rate of butane was lower than that at 116 ppm inlet concentration. The lower elimination rate, at the higher inlet concentration, might be due to a lower residence time or a higher flow rate. As previously discussed, the pollutant absorption might be the rate limiting process for the biofiltration of butane. Thus, with a longer residence time, the butane would be absorbed more completely into the aqueous film attached to the compost material, which in turn, would result in more complete overall elimination of butane.

For inlet concentrations above 200 ppm, the kinetic behavior of butane elimination in the compost biofilter also followed a reaction limited zeroth order kinetics as represented by Equation 1-20. However, the elimination appeared to consist of two distinct processes with two different values for zeroth order coefficients (slopes), as shown in Figure 3-8. For example, at inlet butane concentrations of 240 and 261 ppm, the initial parts of the regression lines had K_o values of 0.89 and 1.08 ppm.s^{-1} whereas the latter parts of the regression lines had K_o values of 2.1 and 1.6 ppm.s^{-1}. The R^2 values of the regression lines were 0.970 and 0.932 for the first parts and 0.998 and 0.999 for the second parts of the lines, respectively. K_o values of 0.89 and 2.1 ppm.s^{-1} correspond to maximum butane elimination capacities of 6.67 and 8.11 g butane.m^{-3}.h^{-1} for the initial processes and 15.76 and 12.01 g butane.m^{-3}.h^{-1} for the final processes, respectively. The average elimination rates of the two part regressions were 9.14 and 10.28 g butane.m^{-3}.h^{-1} for inlet butane concentrations of 240 and 261 ppm, respectively. When compared with inlet concentrations of 116 ppm and 129 ppm, the elimination rates for butane at these higher inlet concentrations (240 and 261 ppm) were higher. Thus, these results indicate that elimination rate of butane through the biofilter increased with increasing inlet butane concentration but the overall percent removal efficiency decreased with increasing inlet butane concentrations. Kampbell et al. (1987) studied removal of propellant mixtures consisting of propane, isobutane and n-butane using a soil biofilter. A laboratory study of the biodegradation of this hydrocarbon mixture resulted in a maximum biodegradation rate of 6.8 mg propellant.kg^{-1}soil.h^{-1} with a first order rate estimation. If the results of the present study of hydrocarbon elimination through a compost biofilter are converted to the same units used by Kampbell et al., the butane elimination capacity of the compost biofilter used in this study was 17.5 mg butane.kg^{-1} dry compost .h^{-1}.

Small-column Biofilter System

Performance during long-term operation

Initial butane concentrations, in the range 5 to 220 ppm, used during continuous operation of small column biofilters are displayed in Figure 3-9. Figures 3-10, 3-11, 3-12, 3-13 and 3-14 show the differences in percent removal by all 10 columns observed during continuous operation. It is seen that Column 3, and not Column 5, resulted in the highest removal efficiency of butane in terms of percent removal.

Compared with the soil filter media of columns 1 and 2 (Figures 3-10 and 3-11), Column 3 (Figure 3-12), which used < 3 mm Gainesville compost, showed a higher percent removal of butane. The soil media did not have as great microbial activities as the compost, see Figure 3-15 for indicators of microbial activity in small-scale column biofilters. Column 4 (Figure 3-13) showed a lower percent removal of butane than Column 3 (Figure 3-12). This might be due to a lower surface area for compost in Column 4 than that in Column 3. To prove this point, about 50 grams of granular activated charcoal were added to Columns 1.2, 2.1 and 4.2 and the capability of these modified filters for removal of butane was observed. Addition of activated charcoal to the biofilter columns enhanced the removal capacity for butane but this effect was temporary lasting only for five days, particularly for Columns 1.2 and 2.1. The low removal efficiency of butane displayed by Columns 1.2 and 2.1 may not have been due to low surface area but rather to lack of microbial activity. However, for Column 4.2., the low removal efficiency of butane was not because of lack of nutrients

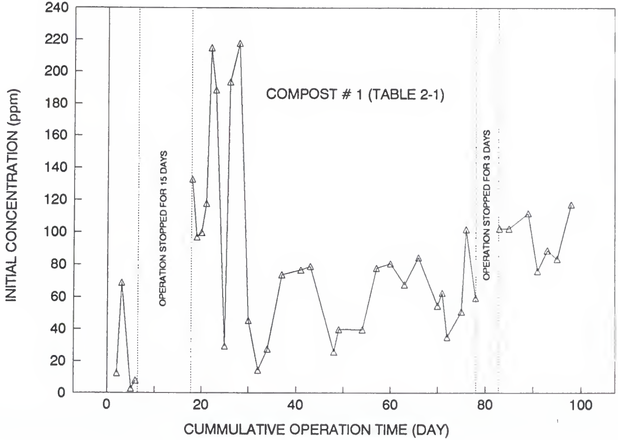


Figure 3-9. Inlet concentrations of butane in continuous operation of small-scale biofilter system.

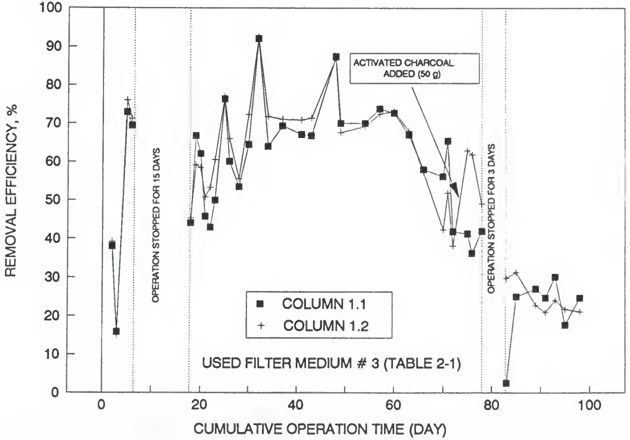


Figure 3-10. Profiles of removal efficiencies during long-term operation of columns 1.1 and 1.2 , small-scale biofilters

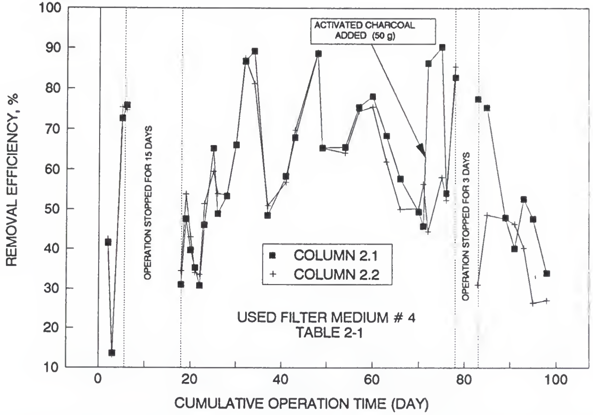


Figure 3-11. Profiles of removal efficiencies during long-term operation of columns 2.1 and 2.2, small-scale biofilter

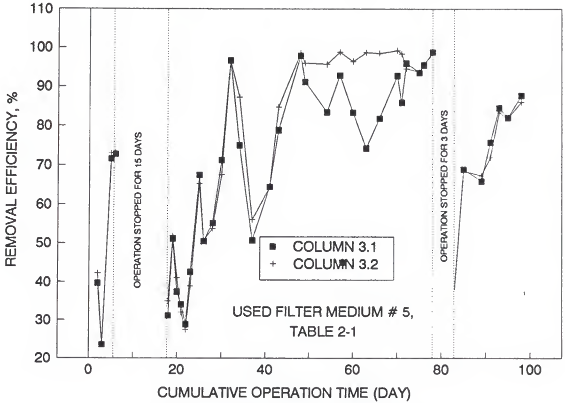


Figure 3-12. Profiles of removal efficiencies during long-term operation of columns 3.1 and 3.2 , small-scale biofilter.

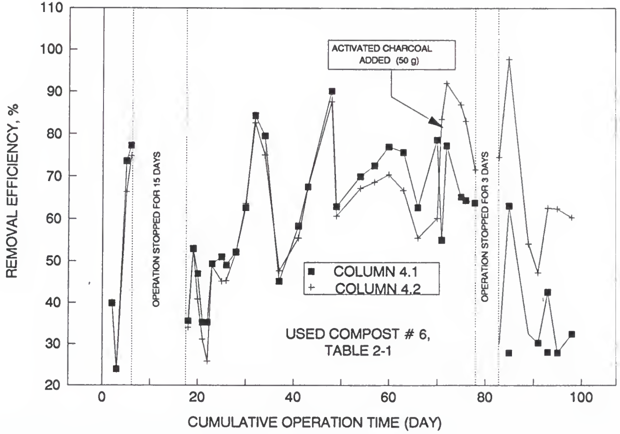


Figure 3-13. Profiles of removal efficiencies during long-term operation of columns 4.1 and 4.2, small-scale biofilter.

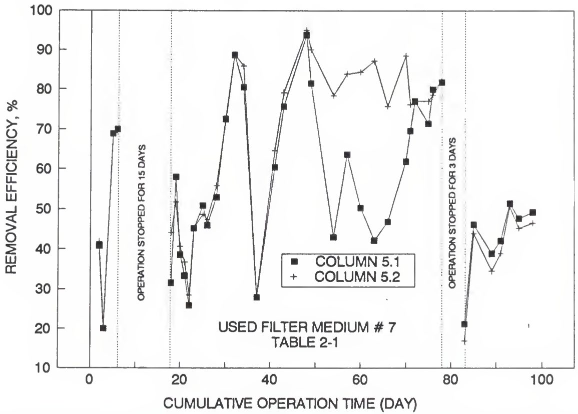


Figure 3-14. Profiles of removal efficiencies during long-term operation of columns 5.1 and 5.2, small-scale biofilter.

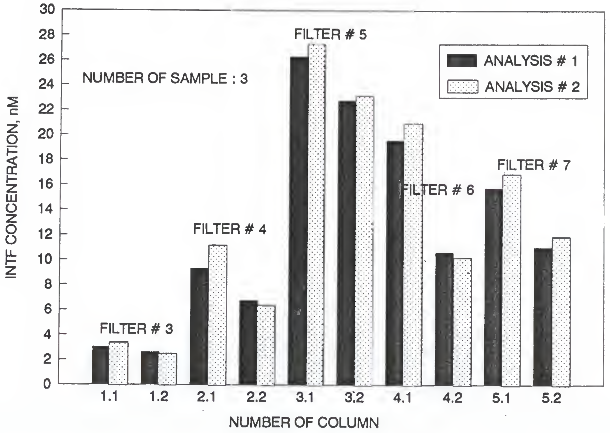


Figure 3-15. Indicators of microbial activity in composts of small-scale biofilters.

or microbial activity but because of low surface area. Consequently, after addition of activated charcoal to the latter column, the elimination of butane increased and remained higher than that observed for other columns with the same compost size but without addition of activated charcoal.

System upset, which was indicated by a sudden decrease in butane removal efficiency, occurred in this experiment. When the operation was stopped for three days, butane removal efficiency decreased considerably. The system needed several days to rebuild the microbial population and recover its optimum performance depending on the type of filter material used. Column 1 that used mostly soil as filter material recovered very slowly, whereas Column 3 that used <3 mm size Gainesville compost recovered faster. System upset might also be affected by a decrease in compost water content that was experienced by all columns. In this study, it was difficult to measure the average compost water content along the small column. Measurement of water content could only be performed at the top of the column filter due to the design and the size of the columns. From visual investigations, however, compost dry-out was seen at the bottom of the columns. Therefore, it was presumed that media dry-out was at least one of the causes that system upset that occurred in columns 1, 2, 3, 4 and 5 after the small filter system operation had been stopped for 3 days.

Effects of compost size and inlet concentration on butane removal

A study of the effects of different compost sizes and different inlet butane concentrations on butane removal was conducted using small-scale biofilter columns. Three different inlet butane concentrations with three replications, were chosen for this study. The sizes of composts/filter materials were based on the original experimental design for the five composts/filter materials, which were assigned to five columns, each with a duplicate. The five composts/ filter material samples selected for use in Columns 1, 2, 3, 4 and 5, were soil, soil + <3 mm size compost, <3 mm size compost, 3-6 mm size compost and 6-12 mm size compost, respectively. Since each type of compost/filter material was arranged in duplicate, the variation within a single compost/filter material, if any, could be studied.

A factorial design method was employed in this particular study. Statistically, factorial design is the most efficient method for studying the effects of two or more variables (Montgomery, 1984). By using a factorial design approach in each complete trial or replication of the experiment, all possible combinations of the influence of the variables (factors) can be investigated. From the data in Table 3-1, for example, the effect of varying inlet butane concentrations can be thought of as the difference between the average response at the first level and that at the second level of inlet butane concentrations. Numerically, this is :

$$\mathit{Inlet\ concentration} = \frac{2248.24}{30} - \frac{237280}{30} = -\ 4.15\%.$$

That is, increasing the variable (factor) inlet concentration from 34.97 ppm to 75.31 ppm causes an average response decrease of 4.15% in butane removal efficiency. Similarly, the main effect of varying compost/filter material size, for example, from column 3 (<3 mm size) to column 4 (3-6 mm size) is :

$$\mathit{Filter\ size} = \frac{116.15}{18} - \frac{1398.96}{18} = -\ 12.93\%.$$

Table 3-1. Data arrangement for factorial design analysis based on percent butane removal efficiency.

A = Inlet Conc., ppm	B = Percent butane removal by five duplicate compost/filter material sizes (indicated by column number)									
	Column 1		Column 2		Column 3		Column 4		Column 5	
35±6.6	87.4	87.0	88.7	88.9	97.9	98.6	90.1	87.7	93.8	95.0
	70.0	67.6	65.4	65.3	91.2	96.0	62.9	60.7	81.5	90.1
	70.1	69.2	65.6	64.2	83.5	95.7	70.0	67.2	43.0	78.4
75±5.6	73.8	72.5	75.5	74.5	92.9	98.9	72.5	68.7	63.7	83.9
	72.7	73.1	78.2	75.5	83.3	96.5	77.0	70.4	50.3	84.4
	67.0	68.0	68.4	62.0	74.2	98.8	75.7	66.7	42.2	87.2
189±12	49.9	60.5	46.2	51.5	42.6	38.9	49.4	48.8	45.2	45.3
	60.1	66.0	48.9	54.0	50.5	50.7	49.0	45.3	45.9	47.3
	53.5	55.6	53.4	53.7	55.1	53.7	52.1	52.0	53.0	55.8

Table 3-2. Analysis of Variance (ANOVA) table for a 3-factor fixed effects model from data presented in Table 3-1.

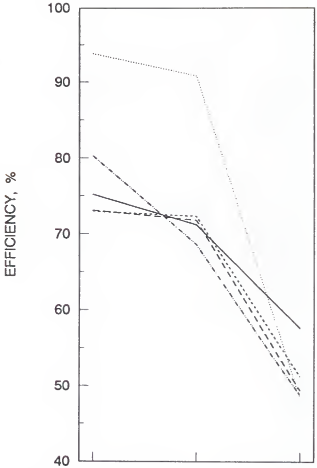
Source of Variance	Sum of Squares	DF	Mean Squares	F_0	$F_{.01}$
Init. conc. , A	13665.12	2	6832.56	86.31	4.98*
Filter mat., B	2061.73	4	515.43	6.51	3.65*
Duplication, C	392.80	1	392.80	4.96	7.08
AB	2044.40	8	255.55	3.23	2.82*
AC	139.71	2	69.85	0.88	4.98
BC	1080.56	4	270.14	3.41	3.65
ABC	918.84	8	114.86	1.45	2.82
Error	4749.60	60	79.16		
Total	25052.75	89			

* significant effect.

That is, the observed difference in changing filter sizes from <3 mm to 3-6 mm causes an average response decrease of 12.93 % in butane removal efficiency.

Two groups of factorial design analyses were performed in this study. The first group of analyses was based on percent removal efficiency and the second group was based on mass removal capacity ($g.m^{-3}.h^{-1}$), where both sets of analyses used the same inlet concentrations. In Tables 3-1 and 3-2 (Page 94) are presented the experimental data obtained and corresponding analysis of variance, respectively, for the data based on percent removal efficiency. Table 3-2 shows that $F_{0.01}$ values for effects of varying inlet butane concentration (A), compost size (B) and the interaction between inlet concentration and compost size (AB) all have values less than the respective F_0 values. It is concluded, therefore, that the effects were significant in varying inlet concentrations, compost particle sizes and their combined interactions in studies on butane removal based on percent removal estimates.

To assist in interpreting the results of these experiments, it is helpful to construct a graph of the average response for each treatment combination, as shown in Figure 3-16. A significant interaction is indicated by the lack of parallelism of the lines. In general, higher percent removal efficiency was attained at low inlet concentrations, regardless of material types/sizes. Changing from low (35 ppm) to intermediate (75 ppm) inlet concentrations, caused the percent butane removal efficiencies to decrease slightly, except for column 5 which contained large compost particles (6-12 mm diameter). Changing from intermediate (75 ppm) to high (189 ppm) inlet concentrations, caused the percent butane removal efficiencies to sharply decrease, where the highest decrease was observed for column 3 (<3 mm compost size). From Figure 3-16 it is seen that column 3 provided more than 90% butane removal



INLET CONCENTRATION, PPM	34.9±6.6	75.3±5.6	189±12
COLUMN 1 FILTER # 3 ———	75.2	71.2	57.6
COLUMN 2 FILTER # 4 - - - -	73.0	72.3	51.3
COLUMN 3 FILTER # 5	93.8	90.8	48.6
COLUMN 4 FILTER # 6 — — —	73.1	71.8	49.4
COLUMN 5 FILTER # 7 —·—·—	80.3	68.6	48.8

Figure 3-16. Graphical representation on percent removal of butane due to the effects of inlet concentrations and filter material types/sizes.

efficiency for an inlet concentration less than 75 ppm, whereas the other columns could only produce butane removal efficiencies between 70 and 80%.

Because the biofilter columns studied consisted of different masses of compost/filter material, even though they occupied the same volume, it is helpful to study the single and multiple effects of varying inlet concentrations and filter/compost sizes using duplications, and assessing their capability for affecting butane removal based on mass butane removal capacity. In Tables 3-3 and 3-4 are shown data obtained and analysis of variance, respectively, based on mass butane removal capacity. As shown in Table 3-4, values of $F_{0.01\,(2,8)}$ and $F_{0.01\,(4,8)}$ are 4.98 and 3.65, which are less than F_0 values for the variables, initial concentrations (A) and types of filter materials (B). It is concluded, therefore, that there were significant effects in the removal of butane in terms of mass removal estimates due to the different inlet concentrations and filter material sizes used. However, it was found that there was no significant effect on the mass butane removal capacity due to interactions between the variables: inlet concentrations and compost sizes, as was encountered in percent butane removal based estimates, as shown in Table 3-2.

In order to assess the individual effects of these variables, a graphical representation of varying inlet concentrations versus mass butane removal capacity for five different compost/filter material sizes is presented in Figure 3-17. In general, changing inlet butane concentrations from low to high values increased the mass butane removal capacity. Filter materials made from soil, and a mixture of soil and small compost particles (<3 mm dia. size) showed the lowest values as well as the smallest increase in mass butane removal capacity. On the other hand, the largest compost size (6-12 mm) represented by column 5, showed a

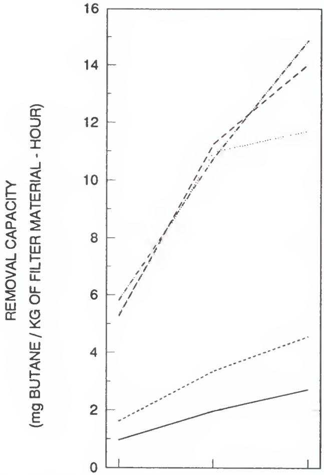
Table 3-3. Data arrangement for factorial design analysis based on mass butane removal.

A = Inlet Concentration, ppm	B = Mass (g/m^3-h) butane removal by compost/filter material sizes as indicated by column number									
	Column1		Column 2		Column 3		Column 4		Column 5	
34.96±6.6	0.86	0.85	1.52	1.52	4.22	4.19	5.04	4.85	5.20	5.26
	1.07	1.03	1.73	1.74	6.10	6.33	5.45	5.20	7.01	7.74
	1.00	0.98	1.62	1.59	5.20	5.88	5.66	5.38	3.45	6.28
75.31±5.6	2.21	2.15	2.92	3.88	12.2	12.8	12.3	11.6	10.7	14.1
	2.10	2.10	3.93	3.80	10.6	12.1	12.7	11.5	8.19	13.7
	1.62	1.64	2.88	2.61	7.88	10.3	10.4	9.08	5.76	11.9
188.6±12	1.00	1.00	1.49	1.36	3.88	3.70	3.80	3.33	3.76	3.59
	5.59	5.77	9.70	9.77	25.3	24.3	31.0	30.6	31.2	32.9
	1.41	1.57	2.51	2.51	6.81	6.37	7.76	7.81	8.91	8.82

Table 3-4. Analysis of Variance (ANOVA) table for 3-factor fixed effects model from data presented on Table 3-3.

Source of Variance	Sum of Squares	DF	Mean Squares	F_0	$F_{.01}$
Init. conc. , A	519.78	2	259.89	6.37	4.98*
Filter mat., B	1232.49	4	308.12	7.55	3.65*
Duplication, C	4.35	1	4.35	0.11	7.08
AB	149.13	8	18.64	0.46	2.82
AC	5.55	2	2.78	0.07	4.98
BC	20.34	4	5.08	0.12	3.65
ABC	16.40	8	2.01	0.05	2.82
Error	2449.17	60	40.82		
Total	4397.20	89			

* significant effect.



INLET CONCENTRATION, PPM	34.9±6.6	75.3±5.6	189±12
COLUMN 1 FILTER # 3 ———	0.96	1.97	2.72
COLUMN 2 FILTER # 4 --------	1.62	3.34	4.56
COLUMN 3 FILTER # 5	5.32	10.96	11.71
COLUMN 4 FILTER # 6 — — — —	5.26	11.25	14.04
COLUMN 5 FILTER # 7 —·—·—·—	5.82	10.74	14.86

Figure 3-17. Graphical representation of dependence of mass rate of removal of butane on variations in inlet concentrations and filter material types/sizes.

steady increase in mass removal with increasing inlet concentration, which was greater than those for medium size compost (3-6 mm) and small size compost (<3 mm). Changing inlet concentration from 175 ppm to 189 ppm butane resulted in a slightly increased efficiency based on mass removal of butane by column 3.

Thus, it can be concluded that for a possible error (α) of 1%, there were significant effects due to the use different inlet concentrations and different filter material/ compost sizes on the removal of butane from both sets of analyses; i.e. based on percent removal and based on mass removal of butane. Also, there was a significant interaction effect observed between inlet concentration and filter size variables on butane removal, specifically that based on percent removal efficiency. From these analyses, it may be concluded that there was no effect on butane removal attributable to duplicates. The latter conclusion means that the duplicates always showed similar (reproducible) butane removal efficiencies during stable operations, where the duplicates employed exactly the same type and size of filter material.

Effect of Butane Loading Rate on Its Removal

One of the most important findings of this research was the determination of the relationship between butane reduction and its loading rate to the biofilter. The butane loading rate is the amount of butane that is introduced to the system per unit volume of the packing material per unit time (g-butane. $m^{-3}.h^{-1}$). The maximum elimination capacity of the compost is the maximum butane loading rate that the compost can tolerate without inhibiting its microbial activity, and is expressed in the same units as those used for butane loading rate.

The maximum butane elimination capacity for a compost was determined at the optimum operating conditions of the system. Butane concentrations in the inlet gas stream were varied during continuous operation of the acclimated biofilter. The butane removal rates (g-butane.$m^{-3}.h^{-1}$) were plotted versus the butane loading rate (g-butane.$m^{-3}.h^{-1}$). The maximum butane elimination capacity of the compost is determined when the curve flattens out (Ottengraf, 1986). The maximum butane elimination capacity of the Compost 1 (Bench-scale column 1) was determined to be 9.0 g butane.$m^{-3}.h^{-1}$ (Figure 3-18). The maximum butane elimination capacity of this compost was very low because of its low capacity for absorption of butane. This compost also produced low percent removal efficiency (<50 %), as shown in Figure 3-1. The elimination data presented in Figure 3-18 show that Compost 2 (Bench-scale column 2) produced maximum butane elimination capacity near 19.0 g butane.$m^{-3}.h^{-1}$.

Biofiltration of Benzene

Three different biofilter systems were constructed for the proposed experiments on biofiltration control of benzene vapor in air. The first system consisted of a three-stage column, which was filled with a compost that had been inoculated with activated sludge. The second system, consisted of bench-scale columns, which initially had been used for treatment of butane. In both systems contaminated air was introduced by evaporating benzene at constant temperature and subsequent dilution with air. For the bench scale column system, one column contained old compost which originally had been employed for butane treatment and the other column contained freshly prepared compost inoculated with activated sludge. The third set of benzene removal experiments used a batch system. The latter was used to

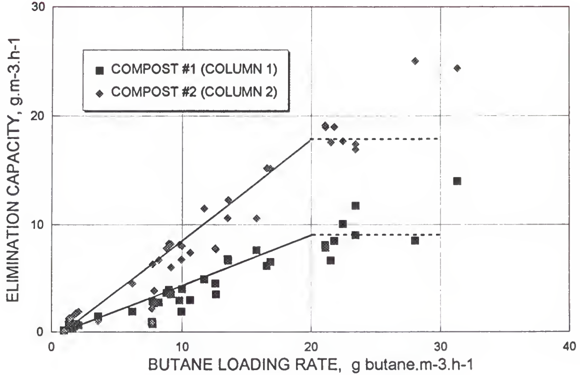


Figure 3-18. Determination of maximum butane elimination capacity of composts 1 and 2 (Bench-scale columns 1 and 2).

study the effects of temperature, compost pH, compost water content and initial benzene concentration on the elimination efficiency and the microkinetics of benzene elimination.

Three-stage Biofilter System

Initial operation

After the column was packed with one and a half year old compost provided by the Experimental Composting Plant of the Agricultural Engineering Department, University of Florida (compost # 8 on Table 2-1, page 40), the conditioning process was initiated by passing air through the biofilter. The same size of compost particles was used for all three columns in the 3-stage column biofilter. About 2.17 kg of wet compost (or 0.83 kg dry compost) had been inoculated with 2 L of secondary activated sludge from Buckman waste water treatment plant, Jacksonville. The conditioning process was necessary to provide enough oxygen flow through the column in order to keep the compost in an aerobic condition.

A week later, benzene was first introduced into the inlet line of the 3-stage biofilter column using a syringe pump. The results of continuous three-stage biofilter operation in eliminating benzene are presented in Figure 3-19. The initial air stream flow was about 2.15 $L.min^{-1}$ and the benzene concentration was about 41 ppm. This benzene concentration was considered to be too high for initial operation even though it resulted in a removal efficiency of about 57 %. The concentration of benzene was then reduced by lowering the dispensing rate adjustment of the syringe pump. The concentration of benzene was adjusted to about 23 ppm at the 34th hour of operation, which produced a removal efficiency of about 67%.

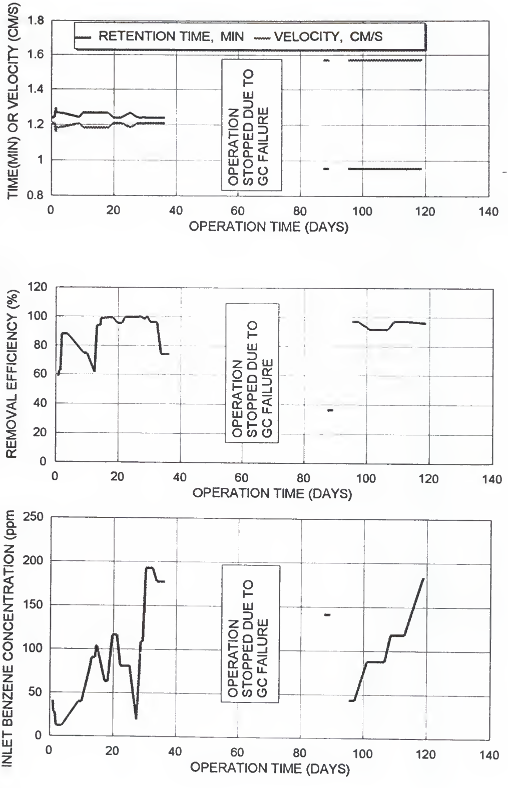


Figure 3-19. Results for the continuous operation of a three-stage biofilter.

Concentration of benzene was reduced further to about 12 ppm at the end of the second day and the removal efficiency was observed to increase to about 88%. When the inlet benzene concentration was increased to about 40 ppm, the removal efficiency decreased again to 75 % and decreased further to 61 % when the inlet concentration was raised to 76 ppm on the 12th day of operation. After this preliminary conditioning period, however, the removal efficiency increased considerably up to 99%, even though the inlet concentration was continuously increased to about 104 ppm, as shown on the 15th day of the operation. It was concluded that the biofilter operation had achieved a stable condition, in about 2 (two) weeks from the start-up time. The inlet concentration was then increased slowly up to about 200 ppm, which resulted in a removal efficiency above 95 % being continuously recorded. From these experiments, it was found that the acclimation period for removal of benzene through a compost biofilter was only 13 days. This result was comparable with acclimation periods for removal of hydrocarbons reported by other investigators (Ottengraf and van den Oever, 1983). The gas velocity used in these experiments was kept constant during this period of operation. During this acclimation period, the velocity was about 1.2 $cm.min^{-1}$, which resulted a residence time of about 1.25 minutes.

On the 34th day of operation however, the removal efficiency of benzene through the three-stage biofilter decreased to 74% for an inlet concentration of 177 ppm. The cause for this decrease in removal efficiency for benzene was apparently due to the compost drying out in the first column. A water content of about 26% on a wet basis was determined in the first (lowest) compost unit, whereas the other two compost stages showed about 60 % water content. Water was added to the first stage compost and the first stage packing was interchanged with the third (top) stage packing. The system was then restarted. At the same time, the syringe was replaced with a large capacity syringe (from 10 mL to 20 mL) and the syringe pump was adjusted to the lowest flow rate. However, the results of gas analyses indicated that the inlet concentration was too high (1745 ppm), even though the removal efficiency at 1745 ppm was still about 70%. Therefore, the original 10 mL syringe was replaced but gas analyses could not be performed due to failure of the pollutant gas analyzer (GC) transformer. Replacement of the transformer was necessary and took about 40 days. However, the system was continuously run at the same conditions until analyses of the sample gas could be performed once again.

Continued operation of three-stage biofilter

After replacement of the GC transformer, the sample analyses of three-stage biofilter column were resumed. However, for the first 3 days of analyses, the results showed that benzene removal efficiencies were low (<40%). Compost water content was then checked and measured from all three columns. Column A (the bottom column) had very low compost water content (± 26 %). Low compost water content of the bottom column compost was first predicted after knowing the result of the sample analysis for removal efficiency. It was confirmed by measuring the difference in weight between the wet and dry composts.

The compost in the 3-stage column was unloaded and appropriate compost watering was carried out in order to meet the desired compost water content. In addition, interchange between stage A (bottom column) and stage C (top column) compost materials was performed. This change was necessary because Stage C might not experience the system upset due to compost dry-out. An adequate water content was determined in the top stage

(C) compost, which explained why stage C showed higher benzene removal efficiencies than those for other lower columns. The inlet for introduction of benzene and air stream into the 3-stage biofilter was changed. Previously, the benzene-air mixture was introduced at the bottom of the three-stage column. In the new configuration, the polluted air stream was introduced at the top of the three-stage column. Also, in the new configuration compost humidification was performed directly from the top of the column using a water trickling system. The drained condensate was collected and reused for compost humidification, knowing that the condensate pH was in the neutral range.

The latter stage of operations of the modified 3-stage column biofilter was carried out after a month. The inlet benzene concentration was initially set at approximately 40 ppm and was continuously increased up to 180 ppm. In this second stage of operation, the linear velocity of incoming air stream was also increased up to 1.55 $cm.s^{-1}$ that resulted in a superficial biofilter retention time of less than a minute. During 30 days of operation, the benzene removal efficiencies were always greater than 90% even though the benzene inlet concentration was increased to 180 ppm.

Kinetics of benzene removal through biofilter

During biofilter operation, sample gas analyses for benzene were performed at all 7 ports of the three-stage column biofilter. Under stable operating conditions, which were indicated by a high removal of benzene, the benzene concentration versus reaction time data were fitted to existing kinetic expression as described in Chapter 1. All rate data except those for inlet concentrations near or greater than 200 ppm, showed that the rate of benzene removal through a compost biofilter followed the expression for reaction and diffusion limitation of a zeroth order elimination process, as described by Ottengraf and van den Oever (1983), see equation 1-25. Examples of data obtained in these kinetic studies are presented in Figures 3-20, 3-21 and 3-22.

At an inlet concentration (Co) of 14 ppm for example, benzene removal kinetics through the compost biofilter followed the expression:

$$\left[\frac{C_o}{C}\right]^{\frac{1}{2}} - 1 = -0.037 - 0.0136\ t$$

with $R^2 = 0.991$ and t is in seconds. Similarly, at inlet concentration of 50 ppm and 84 ppm, the expressions for the kinetic dependencies were as follows, respectively:

$$\left[\frac{C_o}{C}\right]^{\frac{1}{2}} - 1 = 0.024 - 0.0135\ t$$

and

$$\left[\frac{C_o}{C}\right]^{\frac{1}{2}} - 1 = 0.0676 - 0.0138\ t$$

with R^2 values of 0.978 and 0.981, respectively.

Rate coefficient (K_o) values for these three different inlet concentrations were almost identical, i.e., 0.0136, 0.0135 and 0.0138 per second for inlet benzene concentrations of 14, 50 and 84 ppm, respectively. The similarities in values for K_o using these three different benzene inlet concentrations indicated that reproducibility of the kinetics of benzene elimination was very good and appeared to follow the reaction and diffusion limitation .

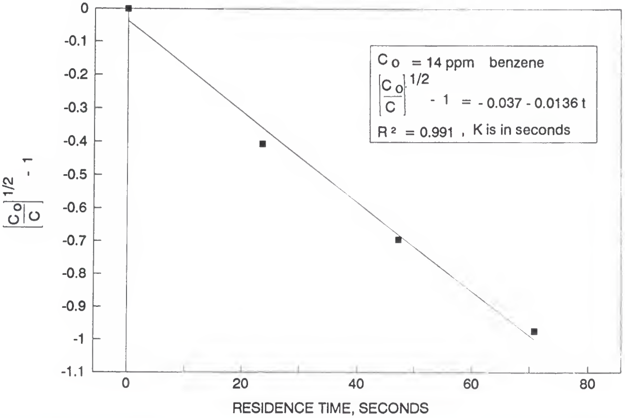


Figure 3-20. Kinetics of benzene removal through biofilter for 14 ppm inlet concentration.

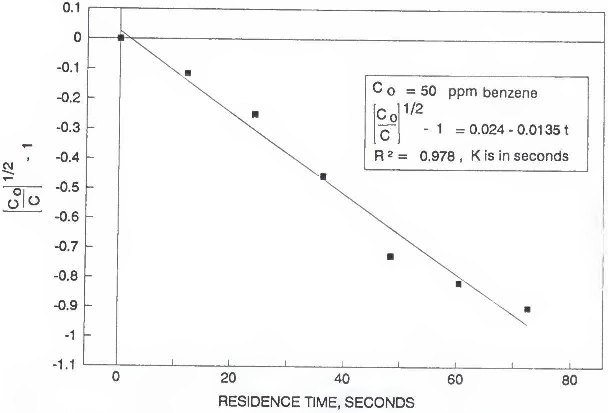


Figure 3-21. Kinetics of benzene removal through biofilter for 50 ppm inlet concentration.

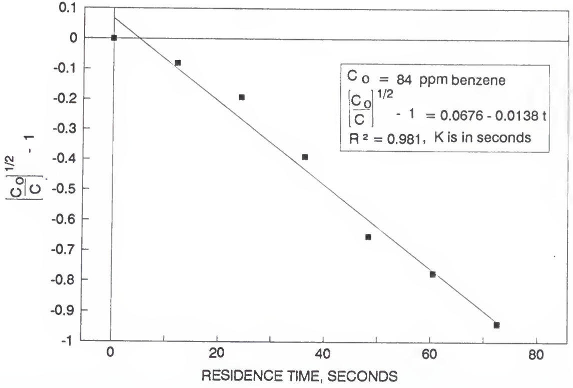


Figure 3-22. Kinetics of benzene removal through biofilter for 84 ppm inlet concentration.

expression developed by Ottengraf.

In order to observe the reaction and diffusion limitations of these studies, a dimensionless plot of concentration versus dimensionless fractional column length was made and the results are presented graphically in Figure 3-23. According to Ottengraf and van den Oever (1983), a linear relationship in Figure 3-23, may be attributed to reaction limitation and the non-linear portion of the plot may be attributed to diffusion limitation. Two situations for benzene removal through the compost biofilter were encountered. The first can occur at a time when there is no diffusion limitation in the wet biolayer. In this case, the biolayer is fully active and hence the conversion of benzene is only controlled by the reaction rate. This situation is defined as "reaction" limitation according to Ottengraf and van den Oever (1983). The second situation is when diffusion limitation occurs in the wet biolayer. This situation may occur when the biolayer is not fully active or in other words, the depth of penetration of benzene in the biolayer is smaller than the thickness of the biolayer. This latter situation is referred to as "diffusion" limitation. Because of these phenomena, the elimination capacity of the biofilter compost is not constant but decreases below a critical value of the gas phase concentration , as shown clearly in Figure 3-23.

A reaction and diffusion limitation mechanism for zeroth order elimination of benzene through a biofilter studied in these experiments appeared to be applicable up to a benzene concentration of 200 ppm. As shown in Figure 3-24, where the inlet concentration of benzene was 203 ppm, the kinetics of benzene removal through the biofilter appeared to follow only a reaction limitation mechanism and zeroth-order elimination. The value of R^2 in the latter case was only 0.93, so that the correlation with reaction limited kinetics was not very strong.

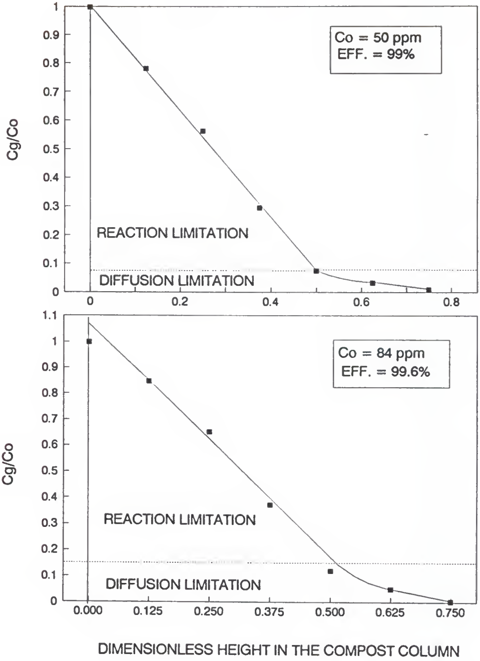


Figure 3-23. Characteristic concentration profile for benzene elimination in a compost biofilter.

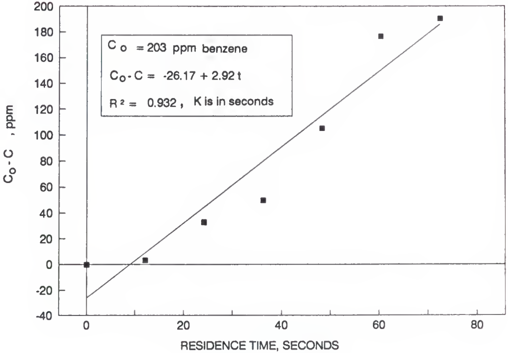


Figure 3-24. Reaction limitation kinetics of benzene removal through compost biofilter.

Calculations of the removal of benzene at this concentration by a reaction and diffusion limitation expression also indicated that the relationship was not strong as well. Thus, it was assumed that at concentrations above 200 ppm benzene, the kinetic dependence of benzene removal through a compost biofilter was in transition from combined reaction and diffusion limited mechanism to a reaction limited mechanism only.

Bench-scale Column System for Benzene

Composts (Composts # 1 and 2 in Table 2-1, page 40) that had previously used for butane elimination in column 1 and column 2 were used for benzene studies, however after several days of operation, the column 1 compost resulted in low removal efficiencies for benzene and the profile of removal was not as good as that from the column 2 compost. As a result, column 1 compost was replaced with new inoculated compost similar to that used in the three-stage biofilter column (compost # 8 in Table 2-1, page 40). Thus, using this arrangement, it was possible to provide additional information on benzene removal through bench-scale biofiltration. First, it was possible to compare removal of benzene and removal of butane, since column 2 of bench scale biofilter was used to remove butane and benzene. Second, it was also possible to observe the differences and similarities of the removal of benzene using a three-stage biofilter column and a single biofilter column.

Initial operation

An introduction of benzene into the bench scale biofilter column was started at an inlet concentration of about 10 ppm with a velocity of about 1.9 $cm.s^{-1}$, which resulted in a residence time of 53 seconds for column 1 and about 45 seconds for column 2. Benzene removal in column 1 was sampled and analyzed on the second day of operation and showed a removal efficiency of only 34% which increased to 63% at the third day. On the fourth day of operation, the benzene removal through column 1 increased further to 71%, however, the profile for benzene removal might indicate that the microbial activity along the column was not homogenous, as shown in Figure 3-25. The operation of column 1 was terminated after a week of operation because the removal efficiency decreased to 48.0 % at an increasing inlet concentration up to 27 ppm.

On the other hand, column 2 showed high removal efficiency for benzene and the removal profile along the column indicated that column 2 compost produced stable and homogenous microbial activities, as shown in Figure 3-26. On the second day of operation for example, column 2 showed 54.0 % removal efficiency for benzene and on the third day, the removal efficiency increased to 96.0 % for an inlet concentration of 11 ppm. On the fourth day the removal efficiency increased to 99.9 % and benzene was almost completely removed at about 55 cm along the biofilter from the inlet, but it was noted that the inlet concentration had decreased to 9 ppm. By the eighth day of operation, the removal efficiency for benzene through column 2 was at 99.0 %, but with an increase in the inlet benzene concentration, the removal efficiency decreased. The further operation it was decided to keep the benzene concentration at a constant value and the biofilter at the same operational conditions since the GC-FID was not available for gas analyses.

Continued operation of bench-scale columns

After replacement of the GC transformer, sampling and analyses of bench-scale column biofilters for treating benzene contaminated air were resumed. Column 1 was loaded with a

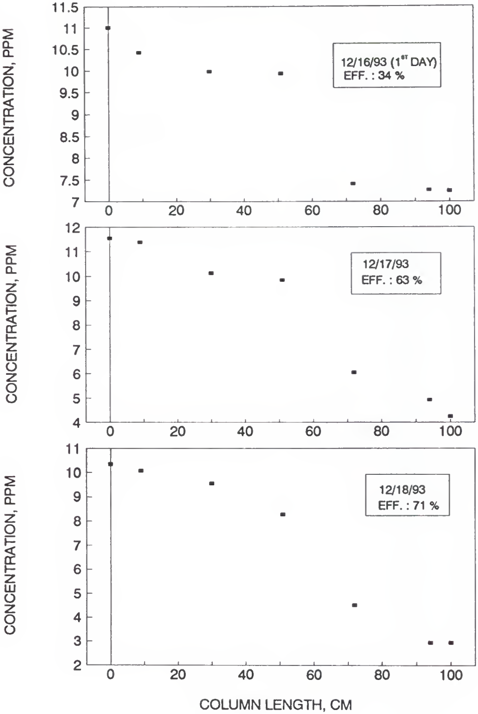


Figure 3-25. Time series profiles of benzene removal through column 1 of bench scale system.

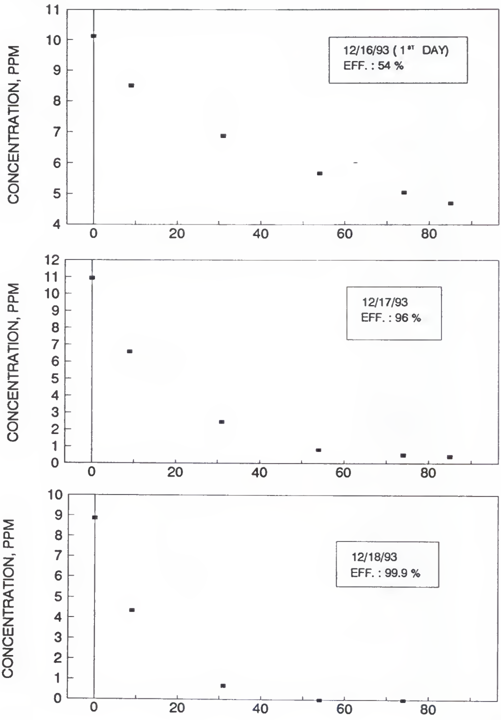


Figure 3-26. Time series profile of benzene removal on column 2 of bench scale system.

fresh compost (# 8) inoculated with activated sludge, as described previously, whereas column 2 contained old compost, which had previously been used to remove butane.

The results of these experiments are shown graphically in Figures 3-27 and 3-28 for columns 1 and 2, respectively. Inlet benzene concentrations were adjusted to different values for each column because the removal efficiencies of the columns were different. The removal efficiency of column 1 was higher than that for column 2 during the second stage of analyses. Inlet benzene concentrations more than 200 ppm were removed by a freshly inoculated compost in column 1 with an efficiency greater than 90%. The compost acclimation period lasted only a few days. The superficial air velocity was increased to about 2.7 $cm.s^{-1}$, which resulted in a retention time of about 0.6 minutes, however, benzene removal efficiency remained greater than 90%. Any further increase in the superficial air velocity and inlet benzene concentration cause a decrease in the removal efficiency. During 30 days of operation, it was found that biofilter column 1 provided benzene removal efficiencies greater than 90% at inlet benzene concentrations of 200 ppm and a superficial residence time of about 0.6 minutes.

Biofilter column 2 on the other hand, showed lower benzene removal efficiencies than biofilter column 1. The maximum inlet benzene concentration was only 100 ppm at a superficial retention time of about 0.5 minutes. For inlet benzene concentration greater than 100 ppm the removal efficiency decreased to about 80%. It should be noted that, during the period when the GC was not available for analyses, column 2 of the bench-scale biofilter system was operated at an estimated inlet benzene concentration less than 50 ppm and a superficial linear velocity near 2.7 $cm.s^{-1}$. The latter conditions suggest that the activity of

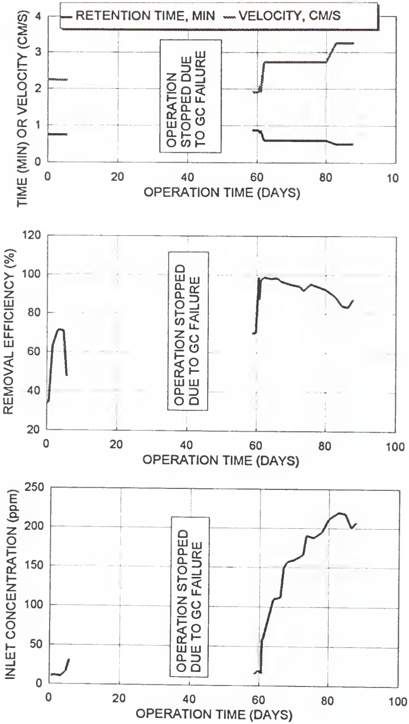


Figure 3-27. Results for the continuous operation of bench-scale column 1 for benzene removal.

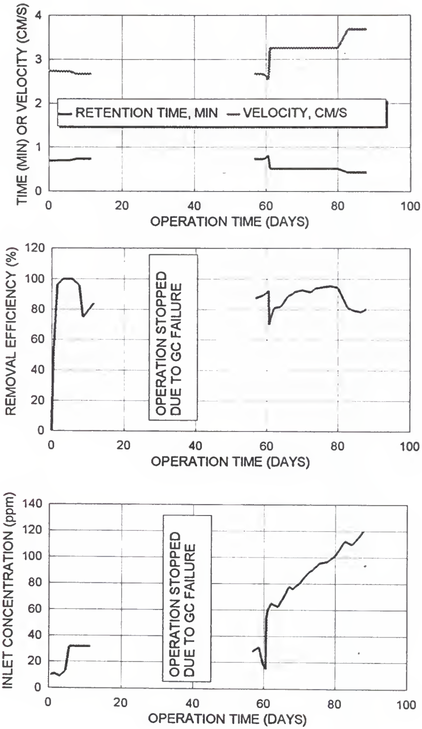


Figure 3-28. Results for the continuous operation of bench-scale column 2 for benzene removal.

benzene degrading microorganisms in biofilter column 2 should be in a stable condition during this period of time. Conversely, column 1 was loaded with a freshly inoculated compost about 2 days before the first sample analysis was performed in the second stage of operations (after replacement of GC transformer). The existing microorganisms in column 1 were due to the inoculation of the sludge and accumulation during acclimation over few days of operation.

The difference in benzene removal efficiencies between columns 1 and 2 might be due to the level of existing appropriate microorganisms for benzene removal. Column 2 compost, which had previously been used to remove butane, might have contained microorganisms that had already adapted to a butane environment. Therefore, it was difficult for the biofilter to adjust to the benzene environment at high inlet benzene concentrations even though at the beginning of the second stage of operation, column 2 had been acclimated to benzene for about 2 months.

It has been reported that the ability of microorganisms to degrade hydrocarbons is not restricted to a few microbial genera; a diverse group of bacteria and fungi have been shown also to have this ability (Atlas, 1981). However, different microorganisms might have different abilities to degrade specific compounds, depending on the previous environment where the microorganisms have lived. For example, Walker et al. (reviewed by Atlas, 1981) examined bacteria from water and sediments for their ability to degrade petroleum. Water samples were capable of degrading petroleum more efficiently than sediment samples even though cultures from both water and sediment samples contained Pseudomonas and Acinetobacter species. In the present study, both columns were initially inoculated with activated sludge. However, the environmental conditions as a result of exposure to either butane or benzene might affect the final microbial population depending whether the microorganisms were butane or benzene degraders. When switching to different pollutants, which might act as a carbon source for microorganisms, it is possible that those microorganisms which may degrade one pollutant, may not effectively degrade another pollutant. As a result, their activity might decrease. This behavior possibly explain why column 2 compost, that had been used previously for butane removal, was less efficient for benzene removal than freshly prepared and activated column 1 compost, which was specifically treated for benzene removal.

Batch System Experiment

Batch experiments in this study were set up in duplicate. Estimated rates of elimination were obtained by averaging the duplicate results over one hour. The variation in duplicate rates was less than 10 %, with about 4 % variation attributed to GC-FID analysis error. Factorial design with a four-fixed effect model was used to analyze the removal efficiency data shown in Table 3-5, and further detailed analyses were accomplished using the orthogonal polynomial method since the data were quantitative (Montgomery, 1984).

From the ANOVA , Table 3-6, it is seen that all environmental conditions except the initial benzene concentration significantly affected the benzene elimination by the compost biofilter. All the interactions except those with initial benzene concentrations also greatly affected the benzene elimination. However, the combined interactions of four adjusted operational conditions, i.e., temperature, water content, pH and initial concentration

Table 3-5. Data on benzene elimination efficiency (%) using batch compost study.

A: Temp. °C	C: pH	Dupli cate	20		40		B: 60		80	
			100	200	100	200	D: 100	200	100	200
5	3	1	77.72	82.65	46.27	49.54	88.19	88.48	42.09	51.82
		2	78.69	79.28	48.27	56.22	92.93	90.15	54.74	56.33
	7	1	90.40	83.09	54.63	52.47	98.42	97.79	52.05	61.74
		2	90.94	90.21	59.21	57.45	98.41	97.76	63.76	65.72
	11	1	64.23	60.46	50.57	53.38	99.60	95.25	66.41	56.58
		2	62.96	50.61	47.80	54.20	99.33	96.33	57.43	60.60
30	3	1	83.60	81.17	86.66	88.76	86.63	84.68	27.01	26.74
		2	82.68	83.66	87.22	87.62	79.51	76.31	41.30	35.47
	7	1	74.69	70.60	92.84	90.77	97.71	98.14	92.12	91.71
		2	77.32	74.41	92.90	92.67	97.72	97.83	93.82	93.38
	11	1	48.50	48.93	83.68	93.22	99.03	99.36	57.74	51.04
		2	53.80	52.70	88.70	85.76	98.63	99.99	87.22	65.89
55	3	1	56.78	49.06	51.60	40.35	37.04	55.79	21.11	14.41
		2	52.41	35.99	25.97	39.48	51.36	53.33	26.47	9.27
	7	1	39.79	48.87	42.96	50.52	62.73	72.59	36.42	22.57
		2	57.99	37.92	38.83	48.01	75.86	67.47	32.79	15.19
	11	1	41.54	52.16	59.79	41.25	73.29	63.97	17.27	17.15
		2	54.02	39.86	19.54	37.63	67.63	67.23	15.82	9.3

A: Temperature (°C); B: Compost water content (%); C: Compost pH; D: Inlet benzene concentration (ppm).

Table 3-6. Analysis of variance (ANOVA) table of the 4-fixed effect model of the factorial design for data in Table 4.1.

Source of Variance	Sum of Squares	Degrees of Freedom	Mean of Squares	F_0	$F_{0.01}$
A	34,329	2	17,165	400.0	4.98*
B	24,488	3	8,163	190.2	4.13*
C	3,434	2	1,717	40.0	4.98*
D	66	1	66	1.6	7.08
AB	7,977	6	1,330	31.0	3.12*
AC	625	4	156	3.6	3.65
AD	71	2	36	0.8	4.98
BC	4,886	6	814	19.0	3.12*
BD	255	3	85	2.0	4.13
CD	19	2	10	0.2	4.98
ABC	4,667	12	389	9.0	2.50*
ABD	270	6	45	1.1	3.12
ACD	33	4	8	0.2	3.65
BCD	51	6	9	0.2	3.12
ABCD	81,614	12	6,801	158.5	2.50*
Error	3,090	72	43		
Total	84,703	143			

* Significant at $\alpha = 1\%$.

A: Temperature (°C)

B: Compost water content (%)

C: Compost pH

D: Initial benzene concentration (ppm).

influenced the benzene elimination. In order to describe the influence of each experimental condition on benzene elimination using the compost biofilter batch system, a graphical representation of the effects of variables are presented and discussed.

Effect of compost water content on benzene elimination

The effect of compost water content (CWC) on benzene elimination was evaluated in conjunction with other variables, such as temperature, compost pH and initial benzene concentration. As shown in the ANOVA, Table 3-6, compost water content (B) had a significant effect on the benzene elimination with a possible error (α) of 1%. Interaction effects between temperature and compost water content (AB), between compost water content and compost pH (BC), and among temperature, compost water content and compost pH (ABC), all showed significant effects on the benzene elimination at α=0.01. The influences of compost pH (3, 7 and 11) and operating temperatures (5, 30 and 55°C), which are presented graphically in Figure 3-29 show that the benzene elimination was a maximum for a compost water content of 60%. For compost water contents of 20 and 40%, benzene elimination decreased considerably and also sharply decreased at a temperature of 80°C. However, when the temperature was fixed at 30°C, the influence of compost pH at a compost water content of 40% also resulted in a high benzene elimination capacity, as shown in Figure 3-29.

From this study it may be concluded that the optimum compost water content was 60% at all conditions influenced by pH, temperature and inlet benzene concentration. At a temperature of 30°C, however, a compost water content of 40% also resulted in a high benzene elimination efficiency. At both 20% and 80% compost water contents, the benzene

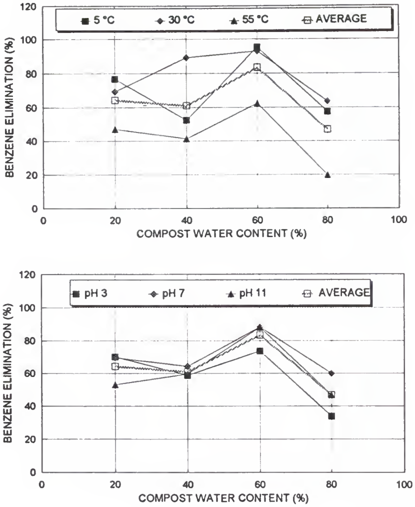


Figure 3-29. Effects of compost water content on the benzene removal in batch experiment as influenced by compost pH and temperature.

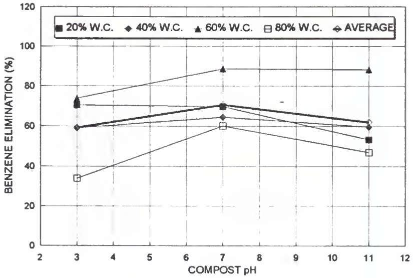
elimination efficiency decreased considerably for all possible combination of temperature and compost pH.

The water content of the filter material (compost) is very important. At too high a water content, that is usually encountered when approaching the maximum water holding capacity of the filter material used, anaerobic zones can develop in the biofilter. Conversely, at too low a water content, the lack of "free" water leads to a loss of microbial activity as well as to a decrease in the gas-liquid transfer rate of the pollutant to the aqueous biofilm, where the biological oxidation (elimination) takes place. Since the elimination of pollutant from the gas stream is due to an absorption mechanism followed by simultaneous microbial degradation in the biofilter and regeneration of product, the water content of the filter medium is a critical parameter. Helmer (Ottengraf, 1986) suggested that from the viewpoint of process engineering, at water contents of the filter material greater than 40%, anaerobic zones could develop. Also, he observed that microbial activity could be reduced at low water contents. It should noted, however that the compounds treated in Helmer's study were odorous organic compounds. Yang (1992), on the other hand, reported that for water contents in the range from 30 to 60% , elimination of hydrogen sulfide gas (H_2S) was high.

The level of water content in the biofilter medium depends on at least two parameters: the type of filter media and the compound being eliminated. Filter media will limit the water content according to their water holding capacity. For example, Kampbell et al. (1987) reported that a water content of only 30% was the optimum value for removal of volatile aliphatic hydrocarbons using soil as a filter medium. Yang (1992) reported an optimum range of water contents between 30 and 60% because the filter material used was yard waste compost. In the present study it was found that for efficient elimination of benzene water contents from 40 to 60% at 30°C were appropriate for yard waste compost. Even though similar types of compost are used as filter materials for biofiltration, the optimum water content can be different due to the difference in the nature of pollutant compounds to be treated. Helmer (from Ottengraf, 1986) suggested using a water content of less than 40% for elimination of odorous organic components, Yang (1992) reported between 30 and 60% water content for elimination of H_2S and this study concluded that water contents between 40 and 60% are appropriate for benzene removal and even higher (80%) water content are acceptable for butane elimination. The differences in the recommended optimum water contents for removal of different compounds might be due to the different solubilities of the compounds in the aqueous film and to the different types of microorganisms that are responsible for oxidizing those compounds.

Effect of compost acidity (pH) on benzene elimination

From the statistical analysis shown in Table 3-6, it was concluded that compost acidity represented by the pH value had a significant effect on the elimination of benzene. In general, a compost pH value of 7 resulted in the highest benzene elimination efficiency whereas both lower and higher compost pH values of 3 and 11, respectively, produced lower benzene elimination efficiencies, as shown in Figure 3-30. Further investigations should be carried out at constant temperature and water content, or with either variable held constant, in order to clearly understand the effects of compost pH on benzene elimination. Figure 3-30 shows that the highest benzene elimination efficiency was achieved for a pH 7 compost at 30°C. However, for compost pH of 11 and a temperature of 30°C, benzene elimination efficiency



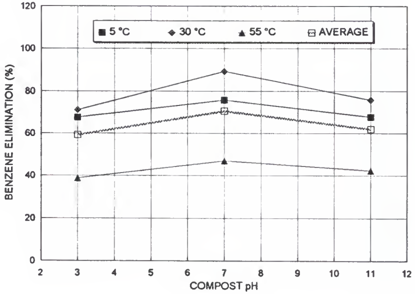


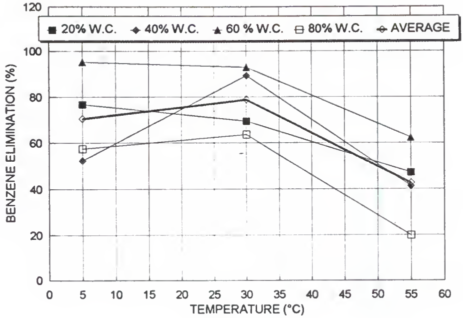
Figure 3-30. Effects of compost pH on the benzene removal in the batch experiment as influenced by compost water content and temperature.

was comparable with that for compost pH of 7 and a temperature of 5°C. At temperature of 55°C, on the other hand, benzene elimination efficiency for all possible compost pH values was always lower than those for other working temperatures (5 and 30°C). There was also an interaction effect between compost pH and compost water content on the benzene elimination efficiency. At all possible temperatures, for 60% water content and neutral (pH=7) compost, the studies mostly resulted in producing the highest benzene elimination. As shown in Figure 3-30, high benzene elimination efficiencies were also observed at both 5 and 30°C, pH values of 7 and 11 and compost water content of 60%. It should be noted that after these experiments had been completed, pH measurements were performed on all the compost samples. The results indicated that a decrease in the compost pH of 11 to a compost pH of 8.5 had occurred. However, neutral (pH=7) and acidic (pH=3) composts were more stable. This pH reduction for the alkaline compost might be the reason that the pH 11 compost removed benzene as well as the pH 7 compost, particularly at 60% water content.

Biodegradation of hydrocarbons normally proceeds by a mono-terminal attack; usually a primary alcohol is formed followed by oxidation to an aldehyde and a monocarboxylic acid (Atlas, 1981). Fatty acids have been found to accumulate during hydrocarbon biodegradation. Sub-terminal oxidation sometimes occurs, with formation of a secondary alcohol and subsequently a ketone. These intermediate products might cause a decrease in the pH for an alkaline compost as observed in this study. Another reason for pH reduction of high pH compost was probably physical reaction occurring during the absorption mechanism that allowed a transfer of higher pH aqueous film from the particle surface into a lower pH aqueous film in the pores inside the compost particles. As a result, the total pH in the aqueous film decreased considerably, leading to a higher removal efficiency for benzene.

Effect of temperature on benzene elimination

Benzene removal efficiencies through a compost biofilter were high at temperatures of 5 and 30 °C in this study, as shown in Figure 3-31. A detailed analysis of the effects of temperature variation on benzene removal was done by selecting the condition where pH=7 for different compost water contents. An orthogonal polynomial analysis method was used knowing that there was a significant effect of temperature on benzene elimination efficiency. Because three levels of temperature were selected, a quadratic equation was produced. Four different quadratic equations are generated. By applying different values of temperature from 5 to 55°C into these equations, quadratic curves for different water contents were produced as shown in Figure 3-32. In general, Figures 3-31 and 3-32 give comparable results, but Figure 3-32 shows more detail and allow for more precise interpretation. For example, both figures indicate that using a temperature of 55°C resulted in lower benzene elimination efficiency and the highest benzene elimination was obtained for 60% water content compost. However, Figure 3-32 provides a more precise determination of the temperature at which the maximum benzene elimination occurred. From Figure 3-31, it appears that the maximum benzene elimination was at 30°C, but Figure 3-32 suggests that temperatures from 15 to 20°C are optimum. These equations relating operating condition variables are important in order to estimate appropriate operating values for temperature, water content or pH at the maximum elimination working condition. As discussed previously, at 55°C operating temperature, benzene elimination decreased sharply for a combination of the variables; compost pH and water content. It was presumed that low benzene elimination at 55°C was



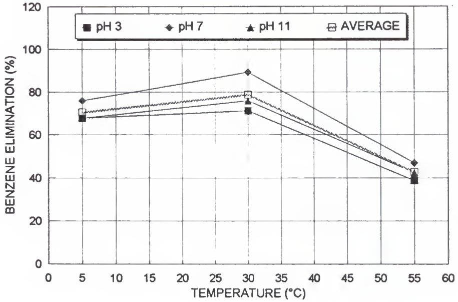


Figure 3-31. Effects of temperature on benzene removal in batch experiment as influenced by compost pH and compost water content.

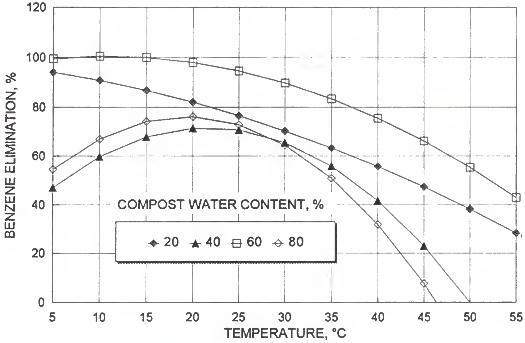


Figure 3-32. Effects of temperature on the benzene removal developed from the equations using orthogonal polynomial method.

due to a vaporization process so that biological oxidation was never completed. A control compost that had been autoclaved and treated the same way as the activated compost sample, also showed a low removal efficiency for benzene at 55°C, as shown in Figure 3-33. At higher temperatures, the aqueous film around the filter particle will evaporate. A a result the benzene vapor that has been absorbed into the liquid vapor may also be released before it is oxidized by microorganisms, i.e. the solubility is decreased. The latter process was detected during a batch experiment when the concentration of benzene vapor in the air space inside the glass bottle after a certain time was constant or even higher than that at a previous sampling time. Even though several gram-negative and gram-positive thermophilic hydrocarbon-utilizing bacteria have been reported to be capable of utilizing hydrocarbons (Atlas, 1981), they are not capable of utilizing light hydrocarbons such as benzene, because light aromatic hydrocarbon are subject to a shift in the pollutant gas-liquid equilibrium to the gas phase and to microbial degradation in the dissolved state. High temperatures in the filter media will reduce the availability of pollutant gas in the aqueous film. Therefore, even though thermophilic microorganisms may exist, they cannot oxidize the target compound in the non-dissolved state as experienced in this study at 55°C. As a result, the overall benzene elimination efficiency at 55°C could always be lower than those at 5 and 30°C. It is noted in this batch study that changing the temperature from 30 to 55 °C did not affect in shifting the group of microorganisms from mesophilic to thermophilic because any group of microorganisms requires a relatively long adaptation time in order for microorganisms to grow in their specific environmental conditions. Thus, the decrease on benzene removal by compost batch experiment at 55 °C might be due to non-biological mechanisms.

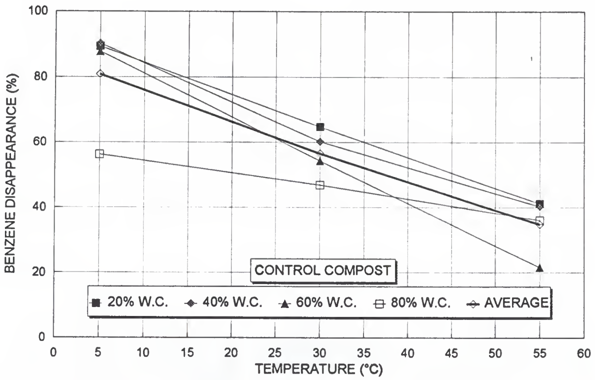


Figure 3-33. Effects of temperature on the benzene disappearance in the autoclaved compost.

Microkinetics of benzene elimination in batch compost experiment

From the results of batch system (static) studies of benzene elimination efficiency, it was decided that benzene elimination experiment at optimum removal conditions should be performed, i.e., at 30°C, pH=7 and 60% compost water content. These detailed experiments were conducted in duplicate at five different initial benzene concentrations in the range from 38 to 845 ppm in duplicate. The results are presented graphically in Figure 3-34.

Using initial benzene concentrations of 38 and 122 ppm, benzene elimination by batch biofilters containing 15 grams compost (dry-basis) was complete in 40 minutes. For initial benzene concentrations of 262, 455 and 845 ppm, the elimination times were about 50, 60 and 80 minutes, respectively. During the first 10 minutes of contact time, benzene eliminations for all benzene concentrations were high, which resulted in relative residual benzene concentrations in the air space from 38 to 50%. This means that more than 50% of the initial benzene was removed in the first 10 minutes of exposure, and then, the rate of benzene elimination decreased considerably depending on the initial benzene concentrations selected.

Benzene disappearance in these sealed bottle (static) compost samples could be due to a variety of mechanisms: sorption by compost components, non-biological transformations, biodegradation, or leakage from the bottles. Rapid benzene elimination during the first 10 minutes of contact with the compost in this study was probably due to the absorption of benzene vapor into the aqueous film of the compost particles. However, after benzene absorption into the aqueous film had taken place, the biodegradation of the benzene vapor by microorganisms became dominant and, therefore, the elimination rate decreased

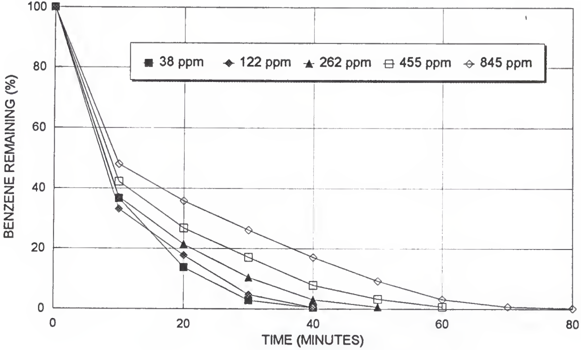


Figure 3-34. Typical benzene disappearance in the compost bath system experiment.
(At temperature : 30°C, water content : 60% and pH = 7)

considerably. Non-biological transformations also might occur in the static biofilter systems but were probably unlikely because the benzene was primarily converted to CO_2, whereas in vitro oxidation was much slower than biological oxidation. Gas leakage was not detected in this experimental study.

Benzene concentrations near 200 ppm were found to be the optimum benzene levels that could be removed by compost in continuous operation of a biofilter both in bench-scale and in the three-stage column system studies. In the batch compost study, benzene concentrations greater than 200 ppm were employed and were found to result in high elimination efficiencies. However, the retention times were much longer in the static batch system studies than in the continuously operating dynamic compost biofilter systems. The geometry of the systems also necessitated a much larger benzene vapor to compost ratio in the batch systems than in the continuous biofilter systems. Furthermore, the air flow through the compost in the continuous system exposed a much larger population of organisms to the benzene vapor. Biodegradation efficiencies, therefore that required minutes in the continuous biofilter system would have hours of contact time available in the batch system study.

The benzene elimination curves in Figure 3-34 show that the batch compost biofilters used in this study very closely followed zeroth-order kinetics as indicated by the linear relationship between fraction of benzene concentration removed and contact time. These results also agreed well with the macrokinetic equations developed by Ottengraf and van den Oever (1983) and which were successfully applied to describing benzene removal using the three-stage compost biofilter system, as discussed previously.

Effect of Benzene Loading Rate on Biofilter Removal Capacity

The maximum benzene elimination capacities for composts were determined after bench-scale columns 1 and 2, and the three-stage column biofilter had been acclimated. All the available data for benzene loading rates and elimination capacities determined when studying those three columns were used to determine the relationship between benzene loading rate and biofilter elimination capacity.

In Figure 3-35 are presented benzene loading and elimination data which show that the maximum benzene elimination of Compost # 2 (in bench-scale column 2), which was previously used for butane removal was about 32 g-benzene.$m^{-3}.h^{-1}$ for a maximum loading rate of 35 g-benzene.$m^{-3}.h^{-1}$. In the case of freshly inoculated compost # 8 loaded in Bench-scale column 1, the maximum benzene elimination, as shown in Figure 3-35, was about 60 g-benzene $m^{-3}.h^{-1}$ for a maximum loading rate of 63 g-benzene $m^{-3}.h^{-1}$. For the three-stage column biofilter system, which was packed with compost # 8, the maximum benzene elimination was determined to be 30 g-benzene. $m^{-3}.h^{-1}$, for a maximum loading rate of 31 g-benzene.$m^{-3}.h^{-1}$.

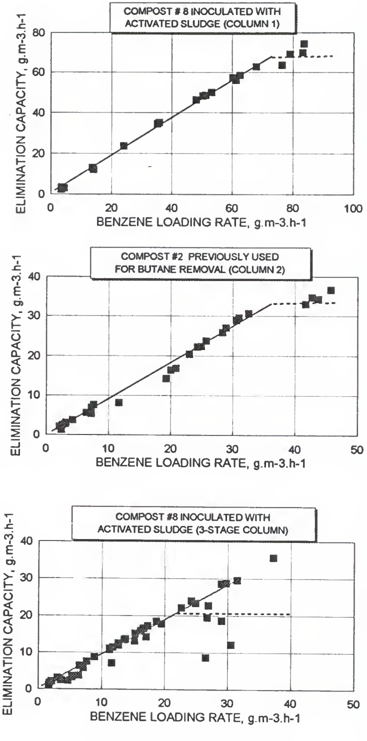


Figure 3-35. Determination of maximum benzene elimination capacity of compost in bench-scale columns 1, 2 and three-stage column.

CHAPTER 4
SUMMARY, CONCLUSION AND RECOMMENDATIONS

Summary

Biofiltration of Butane

Bench-scale and small-scale biofilter systems were used to study removal of butane through compost biofilters. Two different types of yard waste composts were employed in the study of butane removal using bench-scale columns. First, a two year old compost produced by a Gainesville composting plant was loaded into column 1 of the bench-scale biofilter system. Second, a one year old wood chip compost found near Kanapaha waste water treatment, Gainesville, was loaded in column 2. For small-scale columns, five different types/sizes of compost were used. Gasoline contaminated soil from Jacksonville, a mixture of the gasoline contaminated soil and <3 mm size Gainesville compost, <3 mm size , 3-6 mm size and 6-12 mm size Gainesville composts, were used for columns 1, 2, 3, 4 and 5, respectively. Duplicates were set-up for each size/type of the compost, so that a total of 10 small columns were used to study the removal of butane by the small-scale biofilter system. The total period of study for compost elimination of butane , both for bench-scale and small-scale biofilter systems was about 5 (five) months.

For bench-scale biofilter columns, both long term continuous operation as well as kinetic studies were conducted. From these studies, it was observed that a long acclimation period (about 40 days) was necessary for efficient butane removal through a compost biofilter. Stability of operation for butane removal was very difficult to maintain. In order to achieve more than 90% removal efficiency for butane using a compost biofilter, the air stream had to be adjusted to a very low flow rate to provide a sufficiently long residence time. A long contact time was necessary so that the butane in the air stream could be absorbed into the aqueous film at the surface of the compost particles, and for the butane to be microbiologically oxidized by microorganisms in the film.

Use of low flow rates, however was limited by the nature of the compost. A low flow rate of air through the biofilter compost could be achieved only by reducing the compost particle size and by increasing compost bulk density in the biofilter column. However, it should be noted that an increase in bulk density of the compost might reduce the air space of the biofilter bed and, in turn, might create an anaerobic condition if the water content of the compost is at an optimum value (60%). Consequently, this compost condition could upset the activity of the aerobic microorganisms that oxidize the target pollutants, such as butane in this case.

From experimental studies on butane removal using the compost biofilters in bench-scale columns, where the compost consisted of only wood chips, relatively higher removal efficiencies were obtained than in the case where the compost consisted of a mixture of wood chips, leaves and other materials. Inoculation with appropriate natural butane-degrading microorganisms might also enhance the removal of butane. The long acclimation period found for butane removal using compost biofilters in this study might be due to insufficient butane degrading microorganisms being present initially in the compost used. Before the compost was packed in the biofilter column for study of butane removal, it was inoculated with activated sludge from the Buckman wastewater treatment (BWWT) plant, in Jacksonville. However, based on analyses performed by the BWWT laboratory, the sludge did not specifically contain butane degrading microorganisms. Several other organic compounds including benzene, were found in the sludge analyses. As a result, a long acclimation period was necessary to obtain efficient butane removal with the compost biofilter even though it was inoculated with activated sludge. When compared with elimination of benzene using compost inoculated with the same sludge from BWWT, the acclimation period for butane removal was much longer. Benzene removal through the same inoculated compost biofilter on the other hand, resulted in a shorter acclimation time (13 days) than that for butane. This shorter acclimation time for benzene removal through the compost biofilter was comparable to reported acclimation periods for biofiltration of other organic compounds (Ottengraf, and van den Oever, 1983). Moreover, the acclimation period found for benzene removal using a freshly prepared and inoculated compost was only 5 days.

There has been no similar investigation of butane removal using compost biofilters, therefore, it is difficult to compare the time required for the biofilter to achieve stable conditions. However, a study of the removal of volatile aliphatic hydrocarbons consisting of butane, isobutane and propane in a soil bioreactor conducted by Kampbell et al. (1987) suggested that the acclimation time was large in laboratory experiments. An operational scale soil biofilter at Johnson Wax, which was used to treat the same mix of hydrocarbons that were studied by Kampbell et al., was found to have an acclimation time near 20 days.

Also, Kampbell et al. (1987) reported that Hoeks had observed an acclimation period of 30 days for a soil reactor used to degrade natural gas.

After the biofilter acclimation period had been achieved in this study, butane removal through the compost biofilter, (column 2) could be maintained at better than 90 % efficiency. However, it was difficult for column 1 of the bench-scale biofilter system to maintain a stable operational condition at removal efficiencies greater than 90%. When the inlet concentration of butane was increased to more than 200 ppm, the butane removal efficiency decreased considerably. In addition, when the air stream flow rate was increased, the butane removal efficiency decreased sharply at either the same inlet concentration or at a lower inlet concentration for a corresponding increase in air stream flow rate. From these experiments it was concluded that the removal of butane through a compost biofilter was very sensitive to changes in the air flow rate.

High flow rates of the polluted air stream into the biofilter cause a low residence (contact) time for the pollutant in passing through the biofilter column. As a result, butane did not have enough time to absorb on the surface of the compost particles. Kampbell et al. (1987) reported that the residence time for mixtures of butane, isobutane and propane in their soil biofilter was 15 minutes. In the compost biofilter experiments reported here, the maximum residence time for butane was about 2.5 minutes and could not be extended to longer times due to the porous nature of compost.

In the small-scale compost biofilter experiments, different types and sizes of biofilter media were tested at different inlet butane concentrations. In this particular experimental arrangement, the same inlet concentrations of butane were used for all biofilter columns. In this way, it was possible to study the effects of varying inlet concentration on butane removal for several different biofilter media. The use of a factorial design in the selection of experimental variables for statistical analysis made it possible to study interaction effects between inlet butane concentration variables and filter media variables on overall removal efficiency.

During stable operational conditions, three different inlet butane concentrations with three replications, were chosen for this study. Five sizes of composts/filter materials in duplicate were evaluated in the small scale biofilter study. Results indicated that there were significant effects in varying inlet butane concentrations, compost particle sizes and their combination on percent butane removal efficiencies. In general, higher percent removal efficiencies were attained at low inlet butane concentrations, regardless of compost material types/sizes. Changing from low (35 ppm) to intermediate (75 ppm) inlet butane concentrations, caused the percent butane removal efficiencies to decrease slightly. Changing from intermediate (75 ppm) to high (189 ppm) inlet butane concentrations, caused the percent butane removal efficiencies to sharply decrease, where the largest decrease was observed for column 3 (<3 mm compost size). Column 3 provided more than 90% butane removal efficiency for an inlet concentration less than 75 ppm, whereas the other columns could only produce butane removal efficiencies between 70 and 80%.

There were also significant effects in the removal of butane in terms of mass removal estimates due to varying inlet butane concentrations and the filter material sizes used. However, it was found that there were no significant effects on the mass butane removal capacity due to interactions between the variables; inlet concentration and compost size. In general, changing inlet butane concentrations from low to high values increased the mass butane removal capacity. Filter materials made from soil, and mixtures of soil and small compost (<3 mm diameter) showed the lowest removal efficiency values as well as the smallest increase in mass butane removal capacity. A possible reason for low butane removal efficiency by the soil biofilter in this study was that the soil did not contain a sufficiently high population of the appropriate microorganisms, which are responsible for butane degradation. In this case, soil had not been inoculated with activated sludge as was done for the biofilter composts. Also, even though the soil used in this study was contaminated with petroleum (gasoline) products, it might have contained only microorganisms that are responsible for degrading higher molecular weight organic components of gasoline but not lower molecular weight compounds, since the latter may have evaporated from the contaminated soil some time ago. From these results, it might be concluded that microorganisms responsible for degrading butane are different from those capable of degrading heavier hydrocarbons.

The largest compost particles (6-12 mm) showed a steady increase in mass removal efficiency with increase in inlet butane concentrations, which was greater than that for medium size composts (3-6 mm) and small size composts (<3 mm). Also, changing inlet butane concentration from 175 ppm to 189 ppm resulted in only a slightly increased mass removal efficiency. From these duplicate analyses, it was concluded that there was little or no effect on butane removal which could be attributable to a lack of precision (duplication) in the data obtained. The latter conclusion originates from the fact that the duplicate studies always showed similar (reproducible) butane removal efficiencies during stable operations, where the duplicates employed the same type and size of filter material.

Kinetic studies of the elimination of butane using a compost biofilter showed that the butane removal rate did not appear to follow only one form of kinetic expression. At low inlet concentrations (< 20 ppm), butane elimination along the column followed first order kinetics. At higher butane concentrations in the range from 20 to 80 ppm, the rate data were fitted to Ottengraf's diffusion and reaction limitation model for zeroth-order kinetics. For inlet concentrations between 100 and 200 ppm, the rate data followed a reaction limitation mechanism and zeroth order kinetics. For inlet concentrations above 200 ppm, the kinetic behavior of butane elimination in the compost biofilter also followed reaction limited zeroth order kinetics. However, the latter condition appeared to consist of two distinct mechanisms having different values for zeroth order coefficients. The maximum butane elimination capacity using the compost biofilter was 17.5 mg butane per kg dry compost per hour.

Biofiltration of Benzene

Benzene elimination by biofiltration was studied using a three-stage, bench-scale column system and batch compost experiments. The same compost material was used for all three stages of the biofilter column. After 13 days of operation, the removal efficiency for benzene in the 3-stage biofilter column increased considerably up to 99%, even though the inlet benzene concentration was continuously increased up to about 200 ppm. It was concluded that the biofilter column operation had achieved a stable condition after 13 days from start-up. This acclimation time was comparable with hydrocarbon removal acclimation periods of biofilters reported by other investigators (Ottengraf and van den Oever, 1983). The gas velocity used in these experiments was kept constant during the initial acclimation period at 1.2 cm.s^{-1}, which provided a superficial residence time of about 1.25 minutes.

During the second stage of operation, the linear velocity was increased to 1.55 cm.s^{-1}, which resulted in a superficial residence time of about 0.9 minutes. The maximum inlet benzene concentration employed during the latter conditions was less than 200 ppm. Stable operation was maintained after the column inlet was changed from the bottom to the top of the column. In the latter configuration, compost watering was achieved by a trickling water system installed at the top of the column. Eluting water was recycled to the top of the column because no pH change was detected.

Initial bench-scale biofilter column studies of benzene elimination used composts that had been previously used for butane elimination. After several days of operation, one of the composts showed low removal efficiencies for benzene and the profile of benzene removal was not as good as that for the other column. As a result, the first compost was replaced with new freshly inoculated compost similar to that used in the three-stage biofilter column. After conditioning, the inoculated compost, showed a high and stable benzene removal efficiency for inlet concentrations up to 100 ppm during 10 days of operation.

All benzene elimination rate data, except that for inlet concentrations near or greater than 200 ppm, showed that benzene removal through the compost biofilter followed a kinetic expression derived by Ottengraf and van den Oever (1983) for reaction and diffusion limitation of a zeroth order elimination mechanism. Rate coefficient (K_o) values for three different inlet concentrations were almost identical, i.e., 0.0136, 0.0135 and 0.0138 per second for inlet benzene concentrations of 14, 50 and 84 ppm, respectively. The similarities in K_o values using three different inlet benzene concentrations indicated that the reproducibility of the kinetic studies of benzene elimination was very good and closely followed the reaction and diffusion limitation expression over a sixfold range of concentrations.

A reaction and diffusion limitation mechanism appeared to be applicable for biofiltration of benzene concentration up to 200 ppm. However, when the inlet concentration of benzene exceeded this value (203 ppm), the kinetics of benzene removal appeared to follow a reaction limited mechanism and zeroth-order kinetics. The value of R^2 in the latter case was only 0.93, so that the correlation with reaction limited kinetics was not very strong. Also, estimates of the removal of benzene at this high concentration by a reaction and diffusion limited expression indicated that the latter relationship was not strong. Thus, it is proposed that at inlet concentrations above 200 ppm benzene, the kinetic behavior of benzene removal through a compost biofilter is in transition from a reaction and diffusion limited mechanism to a reaction limited mechanism only.

From batch system studies, it was concluded that compost water content, pH and temperature significantly affect the benzene removal efficiency through a compost biofilter. Also, the combined interactions of four operational variables, i.e., temperature, water content, pH and initial benzene concentration, influenced the benzene elimination efficiency. Benzene elimination was a maximum for a compost water content of 60%. A compost pH value of 7 resulted in the highest benzene elimination efficiency whereas both lower and higher compost pH values of 3 and 11, respectively, produced lower benzene elimination efficiencies. Benzene removal efficiencies were high at temperatures of 5 and 30 °C in this study but an orthogonal polynomial statistical method, which was used to analyze the data, suggested that temperatures between 5 and 20 °C were optimum for efficient benzene removal.

Benzene elimination curves showed that the batch biofilters also very closely followed zeroth-order kinetics, as indicated by the linear relationship between the fraction of benzene eliminated and reaction time. The latter results also agreed well with the macrokinetic equations developed by Ottengraf and van den Oever (1983) and the results for benzene removal using the three-stage compost biofilter system discussed previously.

Conclusions

Butane

Saturated light aliphatic hydrocarbons such as butane can be eliminated from air streams using compost biofilters. Ninety percent or greater removal efficiencies requires residence (contact) times of at least 2.5 minutes for inlet butane concentration of 200 ppm. Lower required residence time can considerably decrease butane removal efficiency. Acclimation times for compost biofilters used to remove butane are long (~ 40 days), and are much longer than those reported for higher molecular weight hydrocarbons. From the results of bench-scale compost biofilter experiments on butane removal, it was concluded that the absorption of butane in the aqueous film attached to compost particles was the rate limiting step in butane elimination.

Significant effects on butane removal were observed for varying butane concentrations and different filter media. A filter medium of gasoline contaminated soil provided the lowest butane removal efficiency, whereas a small size compost (< 3 mm diameter) inoculated with activated sludge, showed the highest removal efficiency. The kinetic dependences in butane removal by a compost biofilter followed first or diffusion limited zeroth-order relations, depending upon inlet butane concentrations. In general, it was concluded that at low inlet butane concentration, the elimination tended to follow first order kinetics, whereas at high inlet butane concentration the elimination followed zeroth-order kinetics. Maximum rate of butane elimination, as indicated by the slope of the regression line, K, was proportional to the inlet butane concentration.

Benzene

Benzene, a saturated aromatic hydrocarbon, can be eliminated from air streams by compost biofiltration. Residence times of less than one minute can provide for greater than 90% removal of benzene using a compost biofilter. The acclimation time for a benzene specific compost biofilter is about 13 days at inlet benzene concentrations near 200 ppm. Both residence and acclimation times for benzene removal are much less than those for butane. Thus, it may be concluded that the removal of benzene is easier than the removal of butane using a compost biofilter.

The stability of biofilter operation in the elimination of benzene is substantially affected by the ability of the system to maintain an optimum water content. Other variables such as pH, temperature, nutrient availability and appropriate microorganisms also can affect biofilter operation. When the biofilter water content dropped from 62% to 26%, benzene elimination decreased sharply. Once the compost had become dry it was difficult to recover the optimum water content just by spraying the compost with water. Instead, compost should be unloaded from the column and mechanically agitated with water to allow the water to be absorbed.

Benzene elimination using a biofilter compost that had been previously used for butane elimination was not as good as that obtained using a freshly prepared and inoculated compost. The latter was found to eliminate benzene with more than four times the efficiency of the used compost. Thus, it is possible that microorganisms which are capable of eliminating butane and benzene are quite different.

At benzene concentrations less than 200 ppm the kinetic dependence of benzene removal was very specific. The rate of removal followed zeroth-order kinetics and suggested a reaction/diffusion limited mechanism. From the kinetic data, it was concluded, however, that reaction limited mechanism was more dominant than the diffusion limited mechanism under the experimental conditions employed.

The optimum biofilter water content depended specifically on the organic compound being treated and the type of media used in the biofilter. Compounds that have low solubility in water will be difficult to absorb in the aqueous film attached to the media. Therefore, a high water content is required for efficient removal of low solubility vapors. Optimum water content was found to be about 60% for efficient removal of benzene. The optimum temperature for benzene removal by the compost biofilter was 30°C, even though benzene removal efficiency was still high at 5 °C. Compost pH should be neutral for effective benzene removal.

Recommendations

Compost biofilter can be used for effective butane removal from contaminated air streams. However, the stability of the biofiltration process is difficult to maintain. The residence (contact) time required for efficient removal is relatively long compared to higher molecular weight VOCs and, therefore, requires low velocities through the bed. Since attainment of a low velocity is limited by the physical nature of compost, i.e., a medium with a high bulk density is required, compost which has a low bulk density is not completely effective for butane removal. Alternatively, a soil bed is probably more suitable for butane removal because the air stream can pass through the soil at low velocity (Kampbell et al., 1987), although such conditions result in a high pressure drop and will require relatively high energy input for blower operation. The latter reactor will consequently increase the capital and operational costs of the soil biofilter.

Since the solubility of butane in water is very low, a trickling filter or a drip unit may be suitable for butane removal. As previously discussed in Chapter 1, the principle process of a trickling filter operation is similar to that of biofiltration. Instead of just adding enough water to moisten the filter material on the biofilter, continuous water addition is provided in the trickling filter. The latter watering mechanism may increase the absorption of butane into the relatively thick water film of the trickling filter allowing more butane to be oxidized by microorganisms, but could eventually lead to anaerobic conditions.

If a compost biofilter is selected to remove butane, inoculation of the compost with butane degrading microorganisms either from a pure culture or by natural accumulation is recommended. It should be noted however, that butane removal by a compost biofilter may be limited by absorption of the butane into the aqueous film attached to the filter material. Consequently, the filter material (compost) used should have a large surface area for this application. Further investigation of the effects of surface area of the filter media on butane removal may be needed. For example, varying the addition of activated charcoal to the compost to increase the surface area of the biofilter may provide an optimum surface area that can most effectively remove butane from an air stream.

Application of the results of compost biofilter removal of butane may suggest that a similar degree of elimination could be obtained with other light hydrocarbons, such as propane and isobutane. As a result, a compost biofilter may also be effective in eliminating propellant gas mixtures consisting of propane, isobutane and n-butane, which are common air pollutants released to the atmosphere from working environments of contemporary aerosol propellant industries.

Compost biofiltration of benzene in air streams is very efficient. The acclimation and residence times for benzene removal are much less than those for butane. It is recommended that industrial waste water treatment sludge be used for inoculation of the compost in order to enhance benzene removal. Inoculation of compost with a pure culture apparently is not necessary because activated sludge from this source appears to contain the appropriate benzene degrading microorganisms.

Compost biofilters may be used to remove other aromatic compounds, such as toluene and xylene. Their removal efficiencies may be slightly different from one compound to another, because of the differences in the degree of degradability. In order for a compost biofilter to efficiently remove a mixture of benzene, toluene and xylene (BTX), a three-stage biofilter system may be employed. This type of biofilter system may possibly be made to work at optimum performance in eliminating BTX mixtures because each stage of the column may only remove one of the mixture of gases. However, a detailed study regarding BTX removal by a three-stage biofilter needs to be conducted in order to precisely know the effectiveness of such removal.

In general, humidification of the biofilter material is very important in order to achieve and maintain optimum operating condition for biofiltration. Automatic checking and adjustment of compost water content is recommended as a necessary facility for both research and industrial-scale biofilters. Dry-out of compost due to lack of humidification drastically decreases the biofilter performance in hydrocarbon removal. Similarly, with too high water content in the biofilter system an anaerobic condition might be created, which will affect the activity of aerobic microorganisms in degrading volatile organic compounds.

Three different biofilter systems were constructed for the proposed experiments. The first system consisted of a three-stage column, which was filled with a compost that had been inoculated with activated sludge. The second system, consisted of bench-scale columns, which initially had been used for treatment of butane. In this system contaminated air was introduced by evaporating at constant temperature and subsequent dilution. For the bench scale column system, one column contained old compost which originally had been employed for butane treatment and the other column contained freshly prepared compost inoculated with activated sludge. The third benzene removal experiment was a batch system that was used to study the effects of temperature, compost pH, campost water content and initial benzene concentration on the efficiency of elimination, as well as microkinetic benzene elimination.

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Kardono was born in Jepara, the province of Central Java, Indonesia, on July 15, 1953. After graduating from high school in Jepara, he attended the Department of Agricultural Engineering, University of Gadjah Mada, in Yogyakarta, Indonesia, until graduation in December 1978. Since 1980, he has been working for the Agency for the Assessment and Application of Technology (B .P. P. T.), research agency of the government of the Republic of Indonesia, in the area of new and renewable energy conversion and conservation. His experience includes biogas applications for rural areas, wood gasification for electrical energy generation and coal combustion technology. He has participated in several scientific meetings and courses and has published several papers. From 1988 till the completion of his graduate work, he was awarded scholarships and otherwise supported by the Government of Indonesia. In 1990, he completed a Master of Engineering degree in the air pollution program, Environmental Engineering Sciences Department, University of Florida, and continued his Ph. D. studies in the same specialty area.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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